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DEVELOPMENT OF SAMPLING PROCEDURES FOR POLYCYCLIC ORGANIC MATTER AND POLYCHLORINATED BIPHENYLS

T. S. Hermann

Langston Laboratories, Incorporated

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DEVELOPMENT OF SAMPLING PROCEDURES FOR POLYCYCLIC ORGANIC MATTER AND POLYCHLORINATED BIPHENYLS

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After a review of the most promising sampling trains for collecting PCB, BAP and other POM from stationary sources, a decision was made to evaluate the EPA Method 5 train, a train with a cartridge filter and a train developed by Hangebrauck, Von Lehmden and Meeker. Arochlor 1242, pyrene, anthracene, benzo (α) pyrene, benzo (α) anthracene and coronene were selected to determine collection efficiencies. Based on the results from laboratory evaluations, a modified train was developed and subjected to further studies.

The results of critical laboratory and field experiments indicate the sampling train developed on this program could be used to efficiently and conveniently collect BAP, POM and PCB's simultaneously. In the field studies POM materials were detected, identified and quantified in emissions from several stationary sources, including incinerators, a coal burning steam generating plant and a charcoal burning restaurant.

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PREFACE

This final report describes the research program to conduct critical laboratory and field experiments that demonstrate the feasibility of a new procedure for sampling polycyclic organic matter, benzo(α)pyrene, and polychlorinated biphenyls emitted to the atmosphere from stationary sources. This report is written to the U. S. Environmental Protection Agency under Contract No. 68-02-1255.

LANGSTON LABORATORIES, INC.

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Approved:

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President

ABSTRACT

In the early stages of this program, we gathered information from the literature and from experts at the EPA to select the most promising sampling trains for collecting BAP, PCB and other POM from stationary sources. As a result of this information and our meeting at Research Triangle Park, we decided to evaluate the EPA Method 5 train, a train with a cartridge filter and a train developed by Hangerbrauk, Von Lehmden and Mecker. To effectively challenge these trains, we selected Arochlor 1242, pyrene, anthracene, benzo(α)pyrene, benzo(α)anthracene, and coronene. Based on the results from our laboratory evaluations of the 3 trains, we concluded that our newly developed train, which is a modified combination of the Hangerbrauk, Von Lehmden and Mecker train and EPA train, was the most suitable sampling train and selected it for further studies. This decision was justified by challenging the train in laboratory studies by the experiments conducted on 6 stationary source inventories. We refer to this train as the POM train on this contract.

Our general conclusions from an overview of all the laboratory experiments are as follows:

1. Statistically reliable recovery data can be obtained on high level contaminants.

2. These materials can be collected efficiently at low levels, but the precision of sampling is very poor.

3. Recovery is related to the volatility and molecular weight of the particulate being collected.

4. Recovery data on low level contaminants indicated that low level collection and analysis of POM, BAP and PCB's are possible via the procedures developed on this program.

5. Adherence to isokinetic sampling is absolutely essential for efficient recoverability.

6. Even though the test compounds were held at high temperatures in many experiments, a particulate matter cooling effect was observed in the stack which possessed relatively cool walls.

The results of critical laboratory and field experiments indicate that one train, the sampling train developed on this program, could be used to efficiently and conveniently collect BAP, POM and PCB's simultaneously. In all field studies, we detected, identified and quantified POM materials emitted from stationary sources.

Based on the experiences gained from this program and elsewhere, a summary of our ideas and insights are included at the end of this report in regard to suggestions for future related research that should be pursued on POM and PCB collection and sensing.

LANGSTON LABORATORIES, INC.

PROJECT NO. 73-1179

DEVELOPMENT OF SAMPLING PROCEDURES FOR POLYCYCLIC ORGANIC MATTER AND POLYCHLORINATED BIPHENYLS

I. INTRODUCTION

The objectives of this research program were to: (1) conduct a state-of-the-art study of procedures for sampling benzo-α-pyrene (BAP), polycyclic organic matter (POM), and polychlorinated biphenyls (PCB), in air from stationary sources; (2) conduct a critical trade-off study of these procedures based on prevailing conditions at the source, conjunctive analytical methods, statistical parameters and stability-life characteristics; (3) perform critical laboratory studies; and (4) conduct field evaluations of the developed sampling procedures.

A. Polycyclic Organic Matter

1. Effects

According to some estimates, the mortality rate from lung cancer has increased about 30 times since 1900. This alarming increase has occasioned studies into the cause of cancer which have implicated air pollution as one of the possible causes. A portion of the organic material present in the atmosphere, generally as suspended particulates, has been identified as carcinogenic to experimental animals, and these organic carcinogens have been identified in the atmosphere of virtually all large cities in which surveys have been conducted. While it is true that in no case has a suspected organic carcinogen been demonstrated experimentally to produce lung cancer in humans, the identified carcinogenic activity to experimental animals of several organic particulates found in the atmosphere, strongly suggest that these substances may be significant in increasing the human mortality rate.

According to Sawicki[1] the composition of the urban atmosphere is as yet (1967) undetermined, and the vast majority of the constituents are unknown. Certain of the organic compounds present as particulates in the atmosphere have been identified, and several of these have been found carcinogenic to animals. Evidence also exists of other organic compounds as possible carcinogens. The major class of these organic carcinogens are as follows:

Polycyclic Aromatic Hydrocarbons (PAH)
- Benzo(a)pyrene (BAP)
- Benzo(e)pyrene
- Benz(a)anthracene
- Benz(e)acephenanthrylene
- Benzo(b)fluoranthene
- Benzo(j)fluoranthene
- Chrysene
- Dibenzo(e,l)pyrene
- Dibenzo(a,h)pyrene
- Ideno(1,2,3-ed)pyrene

Polynuclear Aza-heterocyclic Compounds
- Dibenz(a,h)acridene
- Dibenz(a,j)acridene

Polynuclear Imino-heterocyclic Compounds

Polynuclear Carbonyl Compounds
- 1,2-Benzanthracene
- 7H-Benz(de)anthracen-7-one

Akylating Agents
- Aliphatic and Olefinic Epoxides
- Peroxides
- Lactones

Promoting Agents
- Phenols
- Long-chain Aliphatic Hydrocarbons

The carcinogenicity of the above organic compounds has been established by many investigators in laboratory experiments.

The major source of atmospheric organic carcinogens is the incomplete combustion of organic matter.[2] A secondary source is the photochemical decomposition of non-carcinogenic organic compounds into

more active compounds. Incomplete combustion occurs, and therefore organic carcinogens are generated, in the process of heat generation, refuse burning, operation of motor vehicles, and several industrial processes.[7,8] Of the compounds generated, the polycyclic organic matter (POM) are the most extensively studied. Of these, benzo-α-pyrene (also known as 3,4-benzopyrene or BAP) is considered one of the most active carcinogen to animals, and consequently, is probably carcinogenic to humans. Much of the literature pertaining to the air pollution aspects of organic carcinogens concentrates on the compound BAP, due in part to its high relative carcinogenicity, and also in part to the fact that its identification on the other known or suspect carcinogens is limited or nonexistent, and in the words of Sawicki,[1] "We have no knowledge as to whether the members of this great number of unknown trace chemicals are innocuous, beneficial, or harmful to life in the concentrations at which they are present in the various nonurban, industrial and urban atmospheres."

2. Types of Organic Carcinogens

a. Polycyclic Organic Matter (POM): POM in our environment evolves from high-temperature reactions under pyrolytic conditions during incomplete combustion of organic matter. The formation of POM during such processes occurs in two distinct types of reactions, viz., pyrolysis and pyrosynthesis. At temperatures above 400-500°C, organic materials are partially cracked to smaller, unstable molecules (pyrolysis). These fragments, mostly radicals, recombine into larger thermodynamically-favored and relatively-stable POM and heterocyclic hydrocarbons (pyrosynthesis).[3]

Badger and his co-workers have studied the pyrosynthesis of POM.[4,5] Their original working hypothesis is illustrated in Figure 1. From this data and information acquired by other investigators, Hoffmann and Wynder[3] have formulated the following concept: The temperature that exists during the burning of organic matter easily breaks single carbon and carbon-hydrogen bonds to yield free radicals. These radicals combine and are dehydrogenated to aromatic ring systems which are relatively stable; only the carbon-hydrogen bonds of these components are broken to any significant extent. Long-chain paraffins, widely found in fuels and plants, serve as special precursors for POM. Badger's original concept of PAH formation was verified by extensive, carefully-designed and executed experiments utilizing C^{14}-labeled precursors. Figure 2 summarizes the steps of BAP pyrosyntheses as they are suggested from the experimental findings. This concept can be extended to include hydrocarbons with uneven carbon numbers since methane also serves as a precursor for POM.[6]

Pyrolysis experiments like these were conducted in a nitrogen atmosphere and have been criticized for not accurately reflecting the conditions that prevail during the actual burning of organic matter.

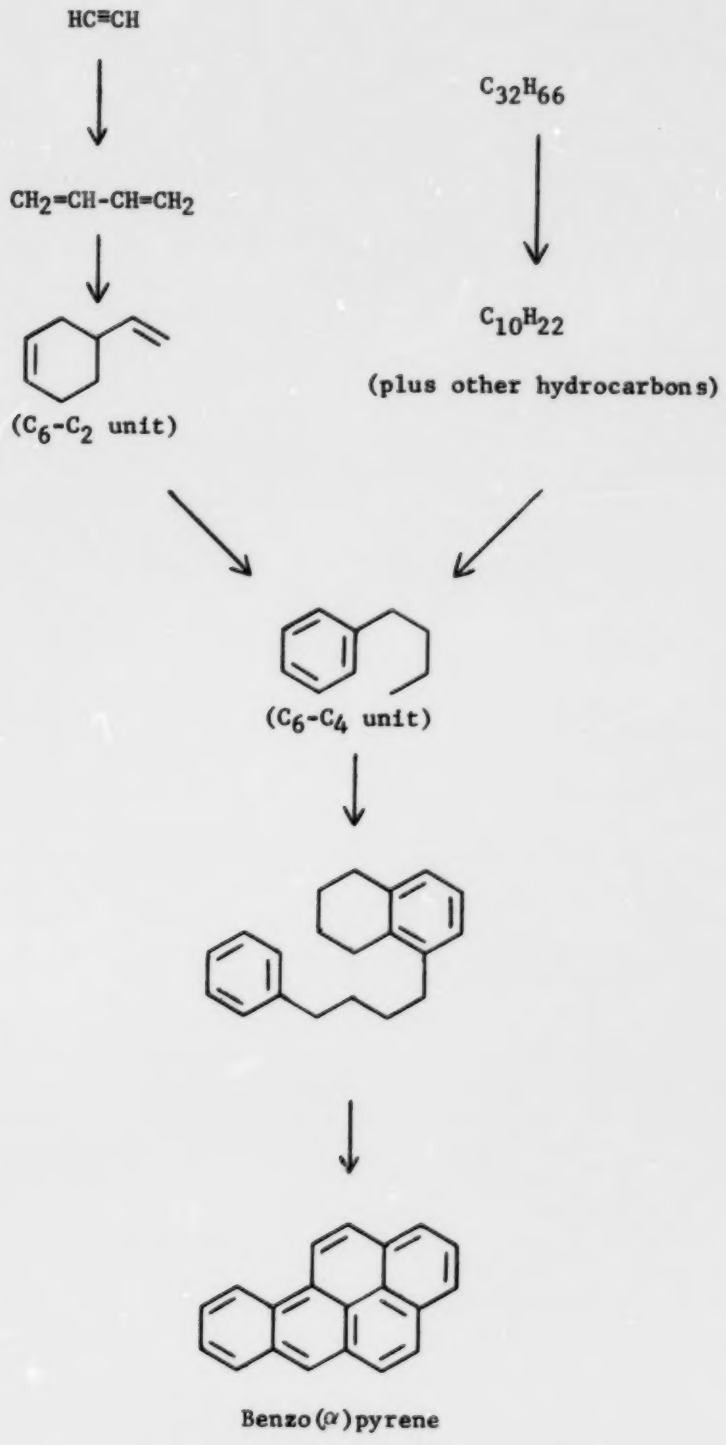


Figure 1 - Benzo(α)pyrene Pyrosyntheses as Suggested by Badger[4]

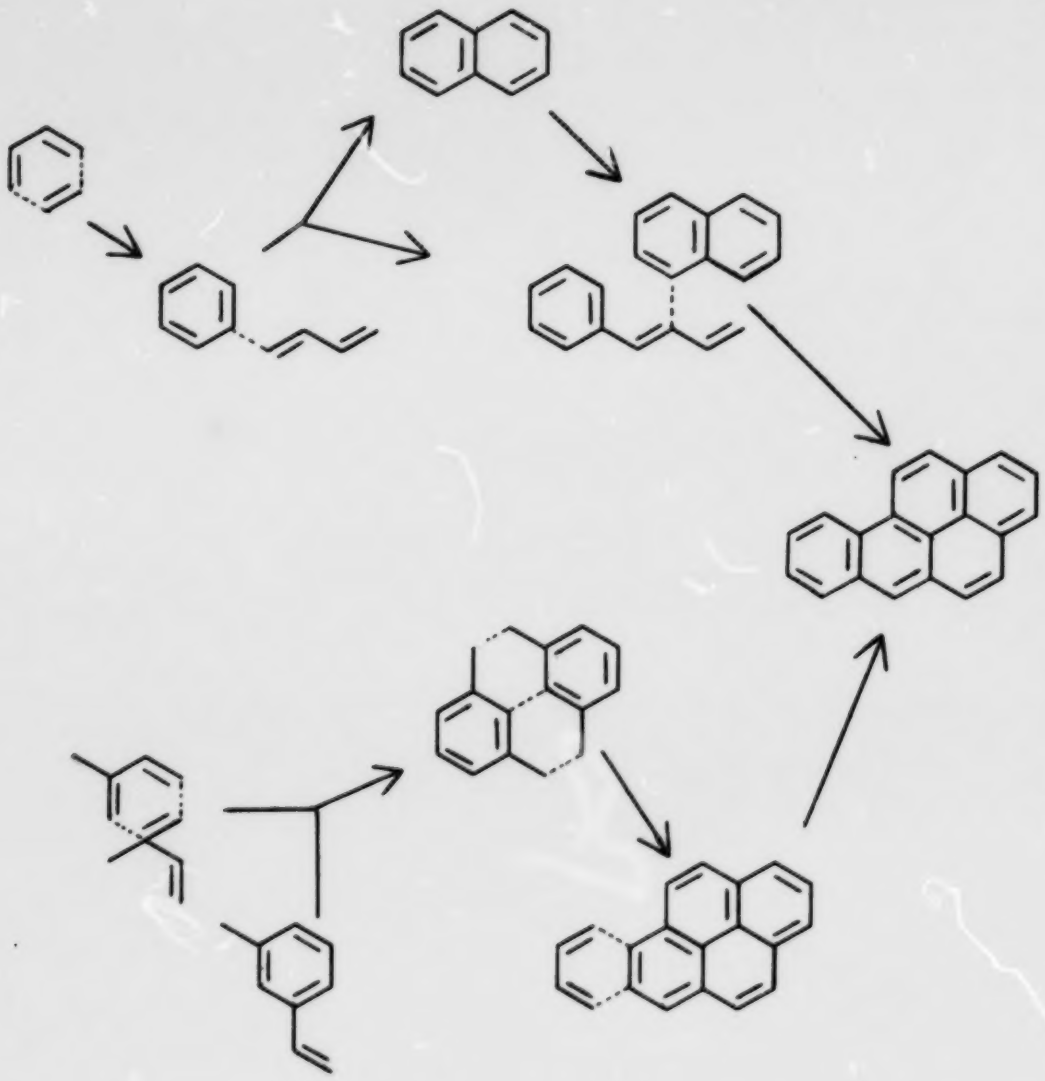


Figure 2 - Pathways for the Pyrosynthesis of Benzo(α)pyrene[3]

As Hoffmann and Wynder[3] point out, the fact remains that these studies agree qualitatively with actual burning conditions of organic matter, and the cited studies were conducted primarily to discover the major precursors and pathways for the pyrosynthesis of PAH rather than to achieve quantitative data.

In actual burning studies of organic matter, a reducing atmosphere must exist around and/or inside the burning cone, as well as inside a combustion chamber to produce POM. This reducing atmosphere is also essential for pyrosynthesis of POM. In addition to the pyrolysis and pyrosynthesis phenomenon, a portion of the POM in our environment also evolves from thermic or catalytic cracking of organic components. The chemical mechanisms leading to the formation of trace amounts of POM by cracking are similar to those occurring during incomplete combustion.

As indicated in Figure 2, other polynuclear aromatic hydrocarbons can be formed by the preceding mechanisms. For example, Long and his coworkers[8] at the University of Birmingham have shown that many POM are formed during incomplete combustion of ethylene and ethane.

POM occur in the atmosphere primarily as adsorbed compounds on soot particles. The biological effect of the carcinogenic agents is critically related to the physical characteristics of the particle. First, particle size predominantly determines the extent to which penetration of the tracheobronchial tree will occur.[9] Particles in the size range of from 0.01 to 2.5 μm are of fundamental biological significance. Those larger than 2.5 μm are primarily arrested in the mucous membranes of the nose, accessory nasal sinuses, pharynx, and oral cavity, assuming they gain host entry at all. At the other extreme, a lesser, but still significant segment of exceedingly small soot particles (less than 0.01 μm) remains suspended in tidal air, except for the minuscule particles precipitated by Brownian movement. The pulmonary retention of particulate matter by the lung in relation to particle size has been given by Dautrebande, et al.[11] To a great extent, particle size also governs the rate and extent of elution of carcinogenic hydrocarbons from the soot particles on which they are adsorbed.

b. Photochemical Pollutants: In addition to the aforementioned POM compounds, certain other classes of POM compounds contain one or more polycyclic functional members. Among these are the photochemical pollutants.

Many photochemical pollutants have been shown to be carcinogenic[11,12] as well as having other physiological effects.[9] In the broadest sense, many diverse compounds are alkylating agents.

A recent source of these compounds has appeared coincidentially with the almost universal use of liquid fuels, such as fuel oil and diesel fuel, in the indirect heating combustion chambers. In the unburned state, these liquid fuels are highly-reactive and when volatilized, undergo oxidation in the presence of oxides of nitrogen in a photochemical reaction. The reaction products consist of a broad group of peroxides, including compounds with polycyclic functions. Unburned vapors in the exhaust products of boilers using a variety of fuels, contain significant quantities of ethylene, propylene, butane, and other unsaturated hydrocarbons.[9,13] Under certain meterological conditions, these vapors react in the presence of sunlight and oxides of nitrogen to form a broad spectrum of highly complex hydrocarbon oxidation products. Interest in compounds belonging to this group has centered primarily around the formation of epoxides because of the demonstrated carcinogenic potency of certain classes of these compounds. However, Cvetanovic[13] studied the decomposition of unsaturated hydrocarbons; the products of decomposition following photochemical reaction include compounds with polycyclic rings.

c. Polynuclear Heterocyclics and Oxygenated Compounds: Large quantities of the aza heterocyclic compounds are found in compounds in some air pollution source effluents,[14] in very low concentration in a variety of exhaust fumes,[15] and in moderate concentrations in the air.[16] Sawicki[1] states that many of these compounds and some others have never been tested for carcinogenic activity; dibenz(a,h)acridene and dibenz-(a,j)acridene and many polynuclear carbazole have been found to be carcinogenic.[17,18]

Hoffman and Wynder note that, in theory, many known nonvolatile "oxygenated substances" may exist in our respiratory environment. One important group of compounds in this group are the polynuclear carbonyl compounds. However, very few chemical studies concerning them have been conducted.

B. Polychlorinated Biphenyls

Evidence of the global ubiquity of polychlorinated biphenyls (PCB) continues to mount.[19] Since the first concern of the persistent stationary source pollutants, PCB's have been found in fowl, fish, eggs, plants, soil, recycled paper and other media in widely dispersed locations. Thus, PCB's, their manufacturing intermediates and their toxic postcursors constitute an increasingly significant class of toxic compounds that may have long-term deleterious effects on humans.

The physical and chemical properties that make polychlorinated biphenyl compounds valuable industrially, assure their ability to become serious, persistent, environmental pollution hazards. These properties

include relatively low boiling points, low water solubility, high dielectric constant, miscibility with organic solvents and polymers, remarkable thermal stability and resistance to chemical degradiation.[49]

Because of these properties, PCB's which are likely to find their way into the atmosphere, eventually enter the human body through the respiratory tract, through the skin, or through foodstuffs which they may contaminate. Residues have been found in human plasma, hair, milk and adipose tissue.

Although PCB residues constitute an important human pollutant burden, no changes in mortality, morbidity or even physiology have been linked to residue levels. Nevertheless, one would expect PCB levels in organs with a high lipid content to be much greater as is the case with the chlorinated hydrocarbon pesticides. Levels may well be high enough to stimulate microsomal enzymes leading to alterations of drug and possibly hormone metabolism. Long-term, low-level exposure effects upon man are unknown, but there is growing concern regarding potential carcinogenic, teratogenic and mutagenic effects. The interactive effects of the various chlorinated hydrocarbon residues with each other are poorly understood, as are their effects upon disease agents. For example, the effect of PCB's upon human virus infections have not been investigated, but PCB's and chlorinated hydrocarbon pesticides act synergistically with duck hepatitis virus. Adverse ecological effects upon birds, shrimp and oysters are also well-established.[49]

Industrial uses may be conveniently classified as closed or consumptive. Closed systems include electrical capacitors and transformers, heat transfer systems and hydraulic fluids. Consumptive uses involve synthetic rubber, paints, plastics, wire insulation, caulking material, flame retardants, cutting oils, pesticide synergists, adhesives, sealants, paper, printing inks and protective coatings for wood, metal and concrete. Inadvertent environmental contaminations can occur accidentally from closed systems, as has been reported recently, but environmental infiltration is inherent in the consumptive uses.[49] Polychlorinated biphenyls may be introduced into the environment from these industrial uses in several ways: by volatilization from commercial products (e.g., coatings); accidental spills (e.g., bursting of transformers); by deliberate discharge of waste; and by volatilization from devices and machines (e.g., PCB discharge from space heaters).

PCB's are, in general, vapors in their normal state when released to the atmosphere. However, as with other vapors, PCB's can be sorbed onto smoke, dust, pollen and other particulate matter.

Unlike the polycyclic organic matter, PCB's are a continuous class of compounds encompassing a diverse spectrum of species. For example, Arochlor 1242 can be characterized by 12 or more peaks on a gas chromatograph, each peak representing one or more specific compounds. Because "fingerprinting" of a given type of PCB is required, great care must be taken in defining the presence of PCB's in the environment.

II. TECHNICAL DISCUSSION OF ANALYTICAL METHODS USED ON THIS PROGRAM

A. Methods of Analysis of Polycyclic Organic

Several publications compare methods and give an overview of the role of analytical chemistry in carcinogenesis (POM) studies.[23-28] The methods of analysis generally consist of the following sequence of steps: (1) Sampling, (2) Extraction, (3) Separation, and (4) Analysis.

1. Sampling Methods

Organic carcinogens (POM) are usually associated with particulates and thus are collected as particulate. While at Litton Industries Dr. Hermann, now with Langston Laboratories, collected POM with "high-volume" air sampler; the particulates (with which the compounds of interest are associated) being collected on a glass fiber filter. Collection into a liquid (cyclohexane) absorbent was employed. The latter collection process continued for many days to obtain sufficient quantities of material. For collecting BAP from high temperature gas streams, the scientists at Langston Laboratories have used water bubblers and condensation traps immersed in an ice-water bath, followed by a high efficiency filter. This sampling procedure proved to be satisfactory for an assessment of BAP from a biological incinerator.

2. Extraction Methods

The organic carcinogens are generally removed from the particulates by solid-liquid extraction, although liquid-liquid extraction, sublimation and distillation (for coal tar mixtures) have also been used.[24]

Solid-liquid extraction: The extraction of airborne particulates is commonly extracted with either benzene or cyclohexane.[24] Other solvents used include chloroform, acetone, isooctane, methanol, dimethylformamide and benzene mixtures of aliphatic hydrocarbons or methanol. The solvent-particulate mixtures can be stirred at a certain temperature or a Soxhlet extraction can be used.

Recent studies have been concerned with the efficiency of extraction. Stanley, et al.,[29] showed that in the analysis of equal weights of air particulates enriched with benzo(α)pyrene, benz(c)-acridene and 7H-benz(de)anthracen-7-one the percentage of these compounds extracted ranged from 50 to 100, 15 to 100, and 40 to 80, respectively. The solvents were cyclohexane, benzene, methylene chloride and acetone.

In another study, Dubois et al.,[30] stated that benzene was of questionable value as an extracting agent for the initial preparation of an air sample. We have found that the larger amounts of material extracted by benzene, as compared with cyclohexane, lead to analytical interferences in the subsequent analyses. Aizina and Mints[31] found similar results in that the extinction of benzo(α)pyrene fluorescence which called for a controlled content of 1,12-benzperylene as an internal standard.

3. Separation

Techniques used for separating the different organic carcinogens include column chromatography, thin-layer chromatography and gas chromatography.[10,24]

a. Column Chromatography: Column chromatography is the common method for separation of a complex mixture of polynuclear aromatic hydrocarbons.

In general, the columns and techniques used are compromises between better separations and analytical speed.[32-37] For example, the cyclohexane elution of an air sample can take 2 weeks and require 500 to 600 fractions totaling 5,000 ml. To speed up the process, it is customary to add increasing amounts of ethyl ether. This speeds the removal of solutes from the column but at the expense of resolution.[33] The chromatographic separation can also be speeded by the use of alumina deactivated by the addition of 1.6 to 1.8% water. Without being deactivated to this extent the PAH would come off the column too slowly.

Hydrocarbons are eluted in the order:[37] aliphatics, olefins, benzene derivatives, naphthalene derivatives, dibenzofuran fraction, anthracene fraction, pyrene fraction, benzofluorene fraction, chrysene fraction, benzopyrene fraction, benzoperylene fraction, and coronene fraction. For example, with alumina containing 13.7% water the pyrene fraction was found in the beginning of the 3% ether eluent; the chrysene fraction followed in the last part of the 3% ether eluent; the benzopyrene fraction appeared in the beginning of the 6% ether eluent, followed by the benzoperylene fraction in the start of the 9% ether eluent and the coronene fraction shortly afterward in the same 9% ether eluent. Although the relative location of the fractions was always the same, unknown variables sometimes caused the fractions to elute sooner or later than expected.

The fractions were fairly well separated, although test tubes containing the tail end of one fraction usually contained small amounts of the next fraction. Most fractions were found in 3 to 6 tubes. However, the benzoperylene and coronene fractions were each spread over 6 to 10 tubes.

Column chromatography studies have also been reported by Sawicki et al.,[34,35] in which the separation of polynuclear aza heterocyclic hydrocarbons and polynuclear aromatic amines was considered. The procedures are essentially the same as for PAH. However, the alumina does cause some decomposition of the amines, e.g., 9-aminoanthracene is recovered in 70% yield as anthraquinone while 2-aminoanthracene is in only 26% yield.

b. Thin-Layer Chromatography: In his review of 1964 Sawicki[24] noted that thin-layer chromatography had been applied only to a small extent in the separation of PAH but would find increased use; since that time there have been a sizable number of thin-layer chromatography (TLC) studies reported.[34,35,38-41] The advantages of this technique are that it is simple, rapid, inexpensive, sensitive, requires little working material, and can resolve complex mixtures.[24]

Various absorbents including silica gel, alumina, cellulose, and cellulose acetate have been evaluated for use in TLC along with differing types of developing solvents. Several authors[33,34,38,39] state that a complete separation consists of extraction followed by column chromatography prior to separation by TLC or paper chromatography and spot location by fluorescence or color development.[40] In the latter study, color development is obtained by the use of 7,7,8,8-tetracyanoquinodimethan which reacts with polynuclear compounds to form pi complexes.

White and Howard[38] give R_F values, the ratio of the migration distance of the substance to the migration distance of the front, for 29 polynuclear aromatic hydrocarbons on cellulose and cellulose acetate adsorbents. Such values, however, are quite specific for a given adsorbent and developing solvent. The R_F values alone are inadequate for characterizing polynuclear compounds.

The efficiency of separation and recovery by TLC has also been studied.[41] Typical results are those reported by Sawicki, et al.,[41] where recoveries of 65% for 9-acridanone, 85% for benzo(α)pyrene were obtained. Assay for these same compounds were also run using fluorometric procedures after TLC separation. It was possible to detect 0.0004 μg of 9-acridanone per cubic meter of air.[41] For benzo(α)pyrene the identification limit ranged between zero and 0.04 μg. Previously Sawicki and Johnson had reported the following identification limits: anthracene - 0.01 μg, phenanthrene - 1.0 μg, fluoranthrene - 0.01 μg, chrysene - 0.01 μg, pyrene - 0.001 μg, and benzo(α)pyrene - 0.001 μg.

The separation and characterization of polynuclear aza heterocyclic hydrocarbons and polynuclear aromatic amines have also been reported. The identification limits are in the same range as for PAH, examples are: carbazole - 0.02 μg, 11H-benzo(a)carbazole - 0.02 μg, 1-azacarbazole - 0.2 μg, and 1,2-dinaphthylamine - 0.1 μg.

c. Gas Chromatography: A limited number of gas chromatography studies have been conducted.[42-47] The procedures are still in the development stage, however, the method promises to be relatively rapid provided the various chromatographic peaks have been identified. As an example of the capabilities of the method the following amounts of PAH in soot have been reported:[42] acenaphthylene - 4,700 μg/g soot, phenanthrene - 5,500 μg/g soot, fluoranthrene - 5,200 μg/g soot, chrysene - 6,300 μg/g soot and benzo(a)pyrene - 2,900 μg/g soot.

d. Other Techniques: Electrophoresis has also been considered as a possible means of separating pollutants after collection.[20,48] The reports showed that separations of polynuclear phenols[48] and of macromolecular material[20] were feasible. However, no quantitative information was given.

4. Analysis

Analyses of the eluate fractions from liquid chromatography and TLC are conducted chiefly via UV absorption measurements or fluorescence measurements.[24] The following discussions briefly review the various analytical procedures which are applicable to the study of airborne carcinogens.

a. Spectral Methods: For the identification and determination of polynuclear hydrocarbons, methods based on ultraviolet-visible absorption spectra and fluorescence spectra play a prominent role. The advantages of absorption spectra are that the wavelength maximum of a compound is unaffected by the presence of other compounds, quenching effects are absent and absorption curves of many polynuclear aromatic hydrocarbons are available in the literature. The main disadvantage, compared to fluorescence, is the lower sensitivity. For many fluorescent compounds the excitation and emission spectra are 10 to 10,000 times more sensitive than its absorption spectrum. The disadvantage of fluorescence spectra are the poorer reproducibility, the fewer available quantitative spectra, and quenching which can drastically affect the sensitivity and shape of the spectral curve.[24]

Several recent articles have dealt with spectral methods. Of these, one was a preliminary communication concerned with the detection of impurities in commercial polycyclic hydrocarbon samples.[21] The remaining articles are concerned with the methods of ultraviolet-visible spectra and fluorescence spectra. The results of our studies are summarized in Table I.

TABLE I

SUMMARY OF RECENT LLI INVESTIGATIONS IN SPECTRAL METHODS

Method	Compound(s)	Procedure	Normal Range of Sensitivity
Ultraviolet	Benzo(α)pyrene	Column Chromatography	1 to 6 μg/ml
Ultraviolet	Dibenzanthrene	Hexane Extraction	0.5 to 5 μg/ml
Ultraviolet	Benzo(α)pyrene	Benzene Extraction	0 to 45 μg/1,000 m^3 Air
Ultraviolet	Benzo(α)pyrene	Hexane Extraction	10^{-2} μg/ml
Ultraviolet	Benzo(α)pyrene Pyrene Perylene 12 Other Aromatics	Modified Piperonal Tests	0.003 μ moles/ml 0.01 μ moles/ml 0.001 μ moles/ml --
Fluorescence	Benzo(α)pyrene Perylene	Acetophenone-Trifluoro-acetic Acid	2.5×10^{-6} M 10^{-6} M
	6 Other Aromatics		--
Fluorescence	Perylene Anthracene Benzo(α)pyrene	Pentane Extraction	0.3 μg/ml 0.3 μg/ml 0.4 μg/ml

b. Other Methods: In one study, Sawicki et al.,[22] investigated the application of the piperonal test to the benzene-soluble fraction of airborne particulates. Piperonal reacts with aromatic compounds to give a colored product which obeys Beer's Law. The correlation coefficients between benzo(α)pyrene concentrations and the piperonal test was 0.95 and 0.89 for 174 urban and 25 nonurban samples, respectively.

Two papers deal with thermochromic tests for determining the amounts of polynuclear compounds containing the fluorenic methylene group and a polycyclic p-quinones. In both cases borohydrides were used at reflux temperatures for color development. Identification limits ranged from 3 to 40 µg. A somewhat similar study was reported where 4-azobenzenediazonium fluoroborate was used to develop color in the determination of aniline, naphthylamine and anthramine derivatives. The identification limits were in the range of 2 to 20 µg.

A direct method of determining BAP has been devised using its characteristic quasi-line emission spectrum at liquid nitrogen temperatures. The method has been used to determine BAP in the air of submarine crew quarters, typically about 1 ppm.

Bioassay techniques have been reported in which the response of a microorganism is correlated with carcinogenic activity. These techniques are based on the phenomenon known as photodynamic action where a combination of light energy and chemical sensitizer (in this case POM) causes the immobilization and death of Paramecium caudatum. Definitive assay for BAP can be performed in the 0.001 to 100 µg/ml region.

B. Methods of Analysis of Polychlorinated Biphenyls

Although methods of analysis for PCB's are available in the literature, nearly all of the papers deal with the analysis of foods, paper products, animal tissues and natural waters. These methods, similar to other standard analytical methods, generally consist of sampling, extraction clean-up, separations and analysis.

1. Sampling Methods

Although we have evaluated at least 10 different sampling techniques for collecting PCB's from air, we have adopted the following procedure:

> We have designed, fabricated and currently use a midget impinger containing 10 ml toluene connected to a battery powered portable sampling pump calibrated to a flow rate of 2.8 ml/min (0.1 cu ft/min).

This unit is a modification of a device manufactured by Unico, Inc.* The total sampling time at each of many sites at a given stationary source for most of our studies is 10 minutes. Thus, the total volume of air collected is 28 liters or 1 cu ft. The final volume is corrected for barometric pressure and atmospheric temperature. The impinger is washed out with an additional aliquot of toluene and analyzed for PCB by direct injection gas-liquid chromatography.

2. Extraction and Clean-Up Procedures

Although we have found that extraction and clean-up procedures are required in the analysis of complex matrices such as paper, tissue, water, etc., for samples collected from air, direct GLC injection of the toluene solutions is carried out in our laboratories.

3. Separations and Analysis

Currently the following method is used to analyze PCB's in our laboratories:

GC conditions for PCB's:

Perkin-Elmer Model 900 Gas Chromatograph*
Detector - Electron Capture (Ni-63)
Column - 4% DC-200 on Anakrome ABS (90/100 mesh)*
(1/4 in. o.d. x 6 ft glass)
Carrier Gas - Nitrogen
Flow Rate - 100 ml/min
Injector Temperature - 230°C
Column Temperature - 180°C
Manifold Temperature - 200°C
Detector Temperature - 200°C

PCB's are qualitatively identified by peak pattern and relative retention data on peaks. We quantitatively measure the major peak area sample versus a known standard.

* Mention of trade name or commercial product does not constitute endorsement or recommendation by EPA.

As an alternative or confirmational method, we employ high pressure liquid-solid chromatography (LSC) under the following conditions:

Perkin-Elmer Model 1220 Liquid Chromatograph*
Detector - UV or RI
Carrier - Heptane or Isooctane
Flow Rate - 1 ml/min (450 psig)
Temperature - Ambient
Column - 5.1 - X or Parasil-ββ' OOPN*

The GLC and LSC methods have been found to be extremely convenient and reliable for many different types of samples including air.

C. Analytical Methods Developed for POM and PCB's on the Project

Because of the problems that were experienced in analyzing POM and PCB's simultaneously in collected samples, we developed a new, very reliable and convenient gas chromatographic method to analyze the materials on this program. The conditions of this method are presented below:

Column - 6 ft x 1/8 in., 6% Dexsil 300 GC on 80/100 Chromosorb "W" H/P*

Carrier - N_2 80 psig, flowmeter at 2.0 mg/min

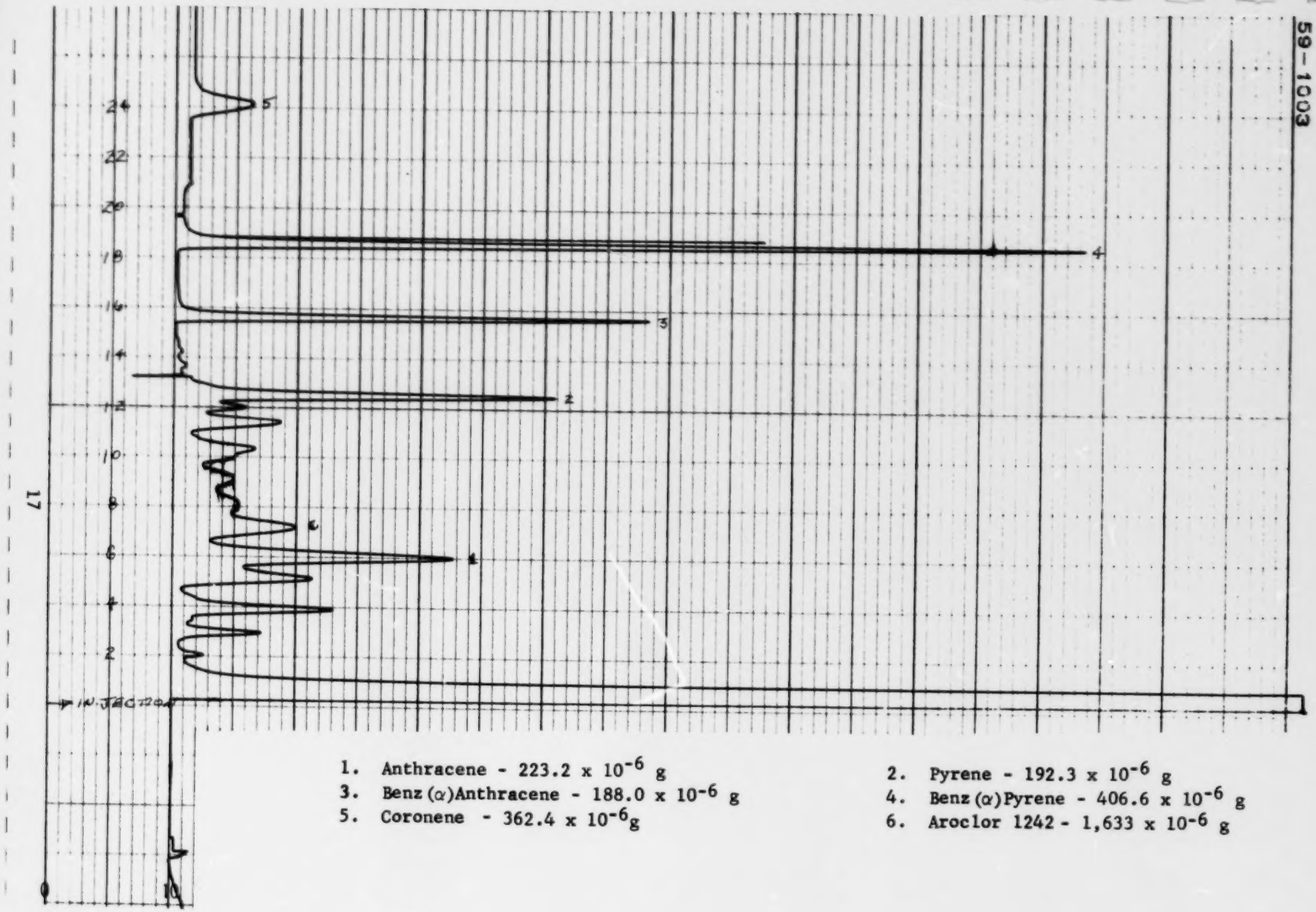
Air - 39 psi H_2 - 35 psi

Program - 1. Start at 170°C hold 8 min.
- 2. 12°C/min to 320°C.
- 3. Hold

Peak Identification -	6 min	223.2×10^{-6} g	Anthracene
	12.4 min	192.3×10^{-6} g	Pyrene
	15.6 min	188.0×10^{-6} g	Benz(α)Anthracene
	18.5 min	406.6×10^{-6} g	Benz(α)Pyrene
	24.1 min	362.4×10^{-6} g	Coronene
	3.1 min	$1,633 \times 10^{-6}$ g	Arochlor 1242

A typical chromatogram is presented in Figure 3 on which is indicated the peaks used for the quantitation of the POM and PCB's.

* Mention of trade name or commercial product does not constitute endorsement or recommendation by EPA.



1. Anthracene - 223.2×10^{-6} g
2. Pyrene - 192.3×10^{-6} g
3. Benz(α)Anthracene - 188.0×10^{-6} g
4. Benz(α)Pyrene - 406.6×10^{-6} g
5. Coronene - 362.4×10^{-6} g
6. Aroclor 1242 - $1,633 \times 10^{-6}$ g

Figure 3 - Gas Chromatograph of POM and PCB's.

III. PHASES I AND II OF THE RESEARCH PROGRAM

A. Objectives

The objectives of this research program were to: (1) conduct a state-of-the-art study of procedures for sampling benzo(α)pyrene (BAP), polycyclic organic matter (POM) and polychlorinated biphenyls (PCB) in air from stationary sources; (2) conduct a critical trade-off study of these procedures based on prevailing conditions at the source, conjunctive analytical methods, statistical parameters and stability-life characteristics; (3) perform critical laboratory studies; and (4) conduct field evaluations of the developed sampling procedures.

From our direct-working experience in sampling and analyzing BAP, POM and PCB in emission gases from stationary sources, we initially studied the sampling procedures of our own design for these materials separately. Even so, these studies were conveniently conducted concurrently. Thus, to attain the aforementioned objectives, this program was divided into five phases: Phase I - State-of-the-Art Study; Phase II - Trade-Off Study; Phase III - Laboratory Evaluations and Recommendations; Phase IV - Field Evaluations and Phase V - Final Report.

At the beginning of the program, these phases, shown in Figure 4, were conducted sequentially but each Phase included the study of each of the three materials concurrently. After initial successes were verified in the laboratory studies, this schedule was changed to the one shown in Figure 5.

B. Phase I - State-of-the-Art Study

Because of our already established expertise, and initial successes in the laboratory on this program, this phase of the program was de-emphasized.

1. Literature Search

The first step of Phase I was to up-date the search of the literature relating to the sampling and analytical chemistry of BAP, POM and PCB. The survey included a critical evaluation of the most recent literature that described the theory and practice of monitoring these materials in gaseous and particulate states in air using manual methods. In addition, a conjugation of abstracts and reprints from all sources such as the open scientific literature, texts and government computer reports were collected. The methods of sampling and analyzing these materials were evaluated critically and economically.

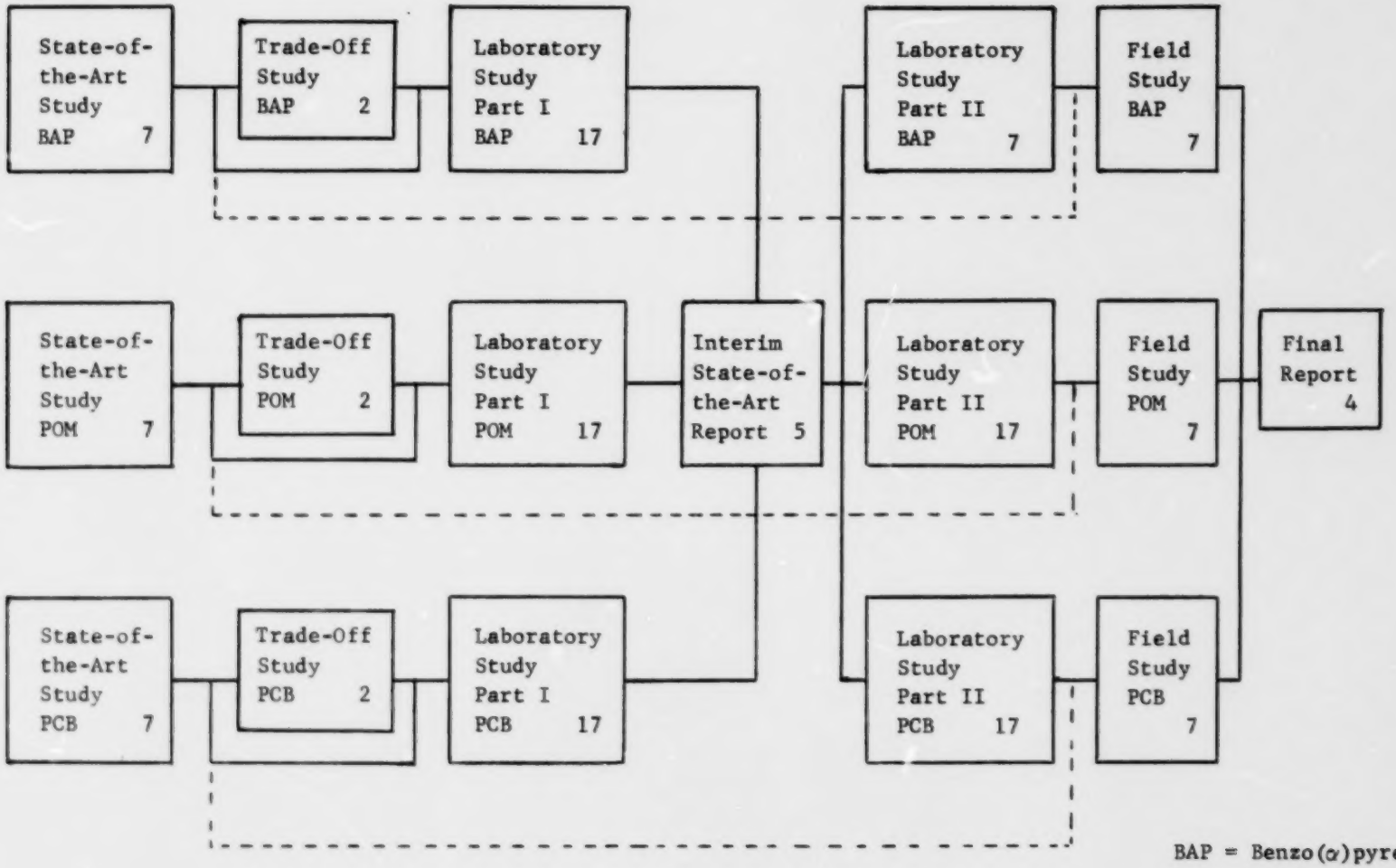

State-of-the-Art Study BAP 7
Trade-Off Study BAP 2
Laboratory Study Part I BAP 17
Laboratory Study Part II BAP 7
Field Study BAP 7
State-of-the-Art Study POM 7
Trade-Off Study POM 2
Laboratory Study Part I POM 17
Interim State-of-the-Art Report 5
Laboratory Study Part II POM 17
Field Study POM 7
Final Report 4
State-of-the-Art Study PCB 7
Trade-Off Study PCB 2
Laboratory Study Part I PCB 17
Laboratory Study Part II PCB 17
Field Study PCB 7

Figure 4 - PERT Chart (Estimated in Weeks)

BAP = Benzo(α)pyrene
POM = Polycyclic Organic Matter
PCB = Polychlorinated Biphenyls

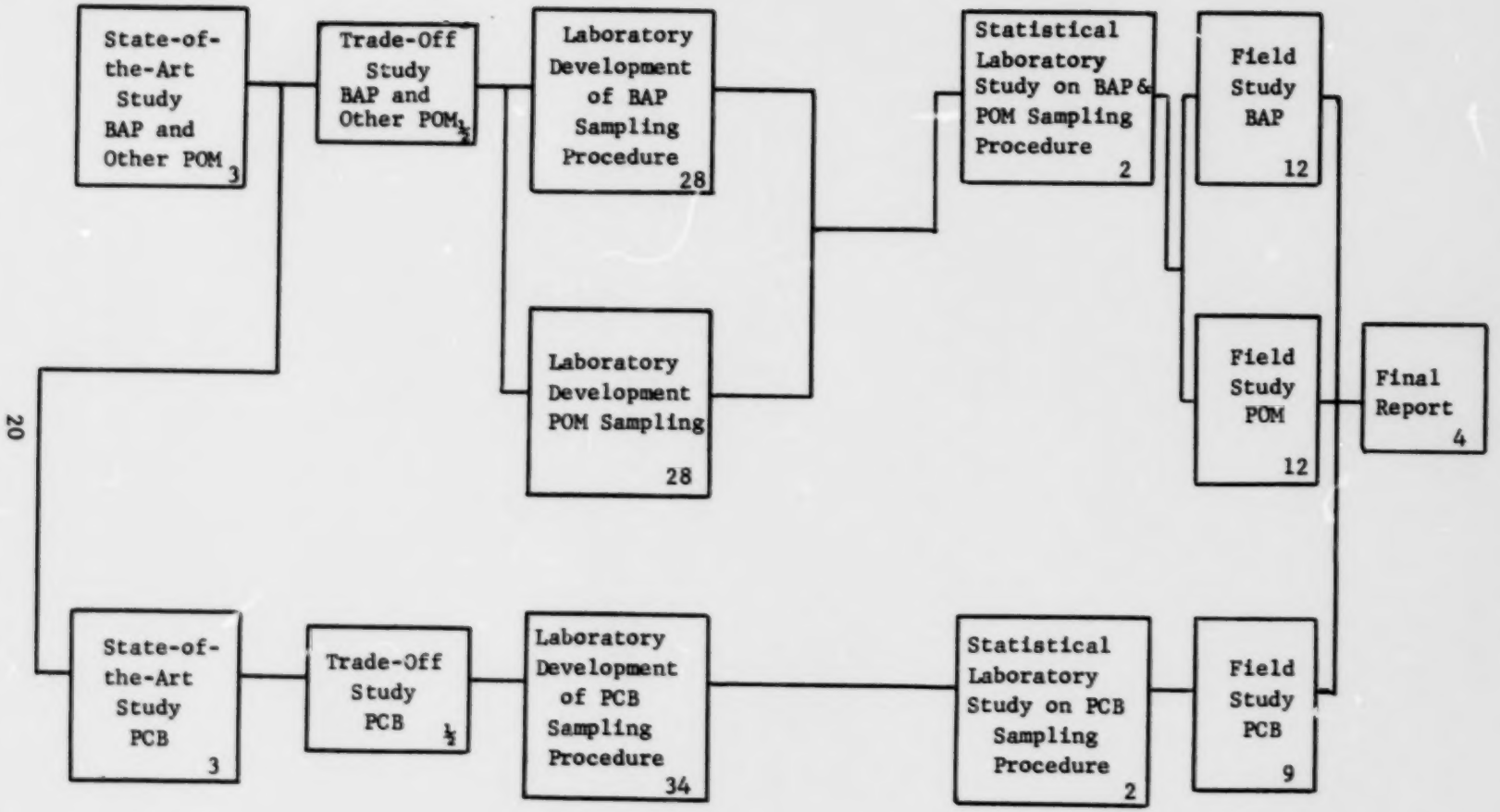

State-of-the-Art Study BAP and Other POM 3
Trade-Off Study BAP and Other POM ½
Laboratory Development of BAP Sampling Procedure 28
Laboratory Development POM Sampling 28
Statistical Laboratory Study on BAP & POM Sampling Procedure 2
Field Study BAP 12
Field Study POM 12
Final Report 4
20
State-of-the-Art Study PCB 3
Trade-Off Study PCB ½
Laboratory Development of PCB Sampling Procedure 34
Statistical Laboratory Study on PCB Sampling Procedure 2
Field Study PCB 9

Figure 5 - PERT Chart (Estimated in Weeks)

BAP = Benzo(α)pyrene
POM = Polycyclic Organic Matter
PCB = Polychlorinated Biphenyls

After all methods were evaluated by the Principal Investigator, a meeting was held with the project officer and other interested EPA scientists to establish other program priorities.

2. Personal Interviews

Subsequently, several EPA scientists who have been particularly active in this area of research, and especially those scientists who have worked directly on analytical methods as evidence through original publications, were selected and interviewed. These interviewees contributed to this program by verifying that our analytical approaches were based on sound scientific principles. They also helped to select the most meaningful test compounds for this program.

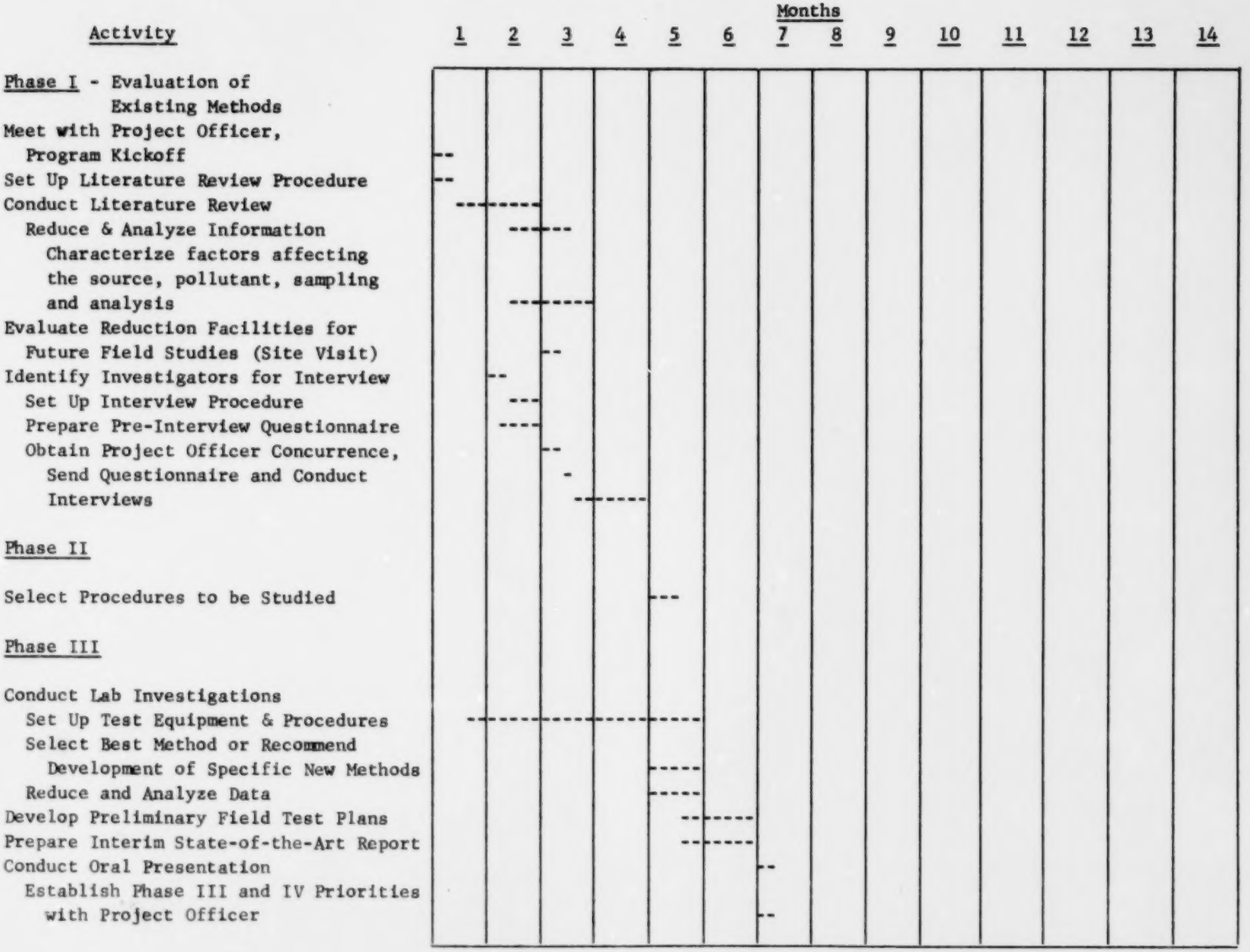
C. Phase II - Trade-Off Study

The information that was acquired in the literature search and from the personal interviews with EPA scientists were reviewed. Subsequently, three procedures were selected for study in laboratory experiments. The key parameters used as the basis of selection were ease of operation, efficiency, compatibility with existing analytical techniques, sampling statistics, stability, cost, required maintenance, and size.

IV. PROGRAM SCHEDULE

As stated above, this research program was divided into 5 major phases, with each phase conducted as indicated on the Program Evaluation and Review Technique (PERT) chart in Figure 4. A graphic portrayal of these phases is presented in Figure 6. The major deviation between the schedule proposed and that followed on this program was brought about by our ability to develop one sampling train early in the program that could be used to efficiently collect BAP, POM and PCB's simultaneously. The program was completed on schedule.

Figure 6 - Program Schedule



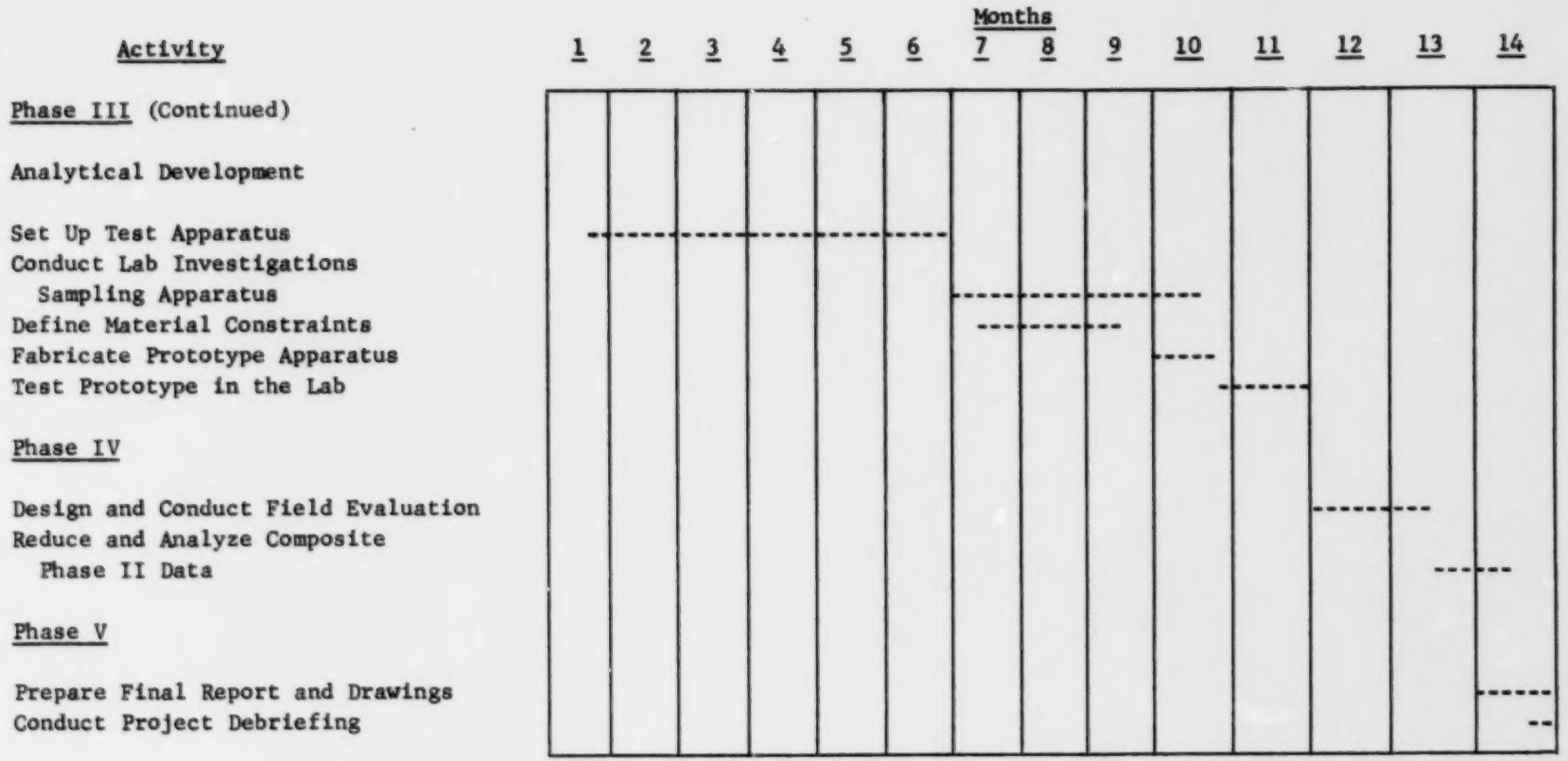


Figure 6 - Program Schedule
(Continued)

V. PHASE III LABORATORY EVALUATION AND RECOMMENDATION

A. Overview

In the early stages of this program, we gathered information from the literature and from EPA scientists to select the most promising sampling trains for collecting BAP, PCB and other POM from stationary sources. As a result of this information and our meeting at Research Triangle Park, we decided to evaluate the EPA Method 5 train, a train with a cartridge filter and a train developed by Hangerbrauk, Von Lehmden and Mecker. To effectively challenge these trains, we selected Arochlor 1242, pyrene, anthracene, benzo-α-pyrene, benzo-α-anthracene, and coronene. Based on the results from our laboratory evaluations of the 3 trains since July 1973, we concluded that our newly developed train, which is a modification of the Hangerbrauk, Von Lehmden and Mecker train, was the most efficient train and selected it for further studies in the laboratory. This decision was justified by laboratory studies and experiments conducted on stationary source stack gases. We refer to this train as the POM train.

As shown on the PERT diagram in Figure 5, we have completed the statistical laboratory studies of the POM train and 6 field studies. The PERT diagram does not reflect the fact that we have developed one train--a modification of the standard EPA Method 6 train--which efficiently collects BAP, PCB and other POM concurrently.

During these studies, 128 experiments were conducted. These experiments which are described in Section VI of this report, were conducted to demonstrate the precision and recoverability of BAP, POM and PCB's. A summary of these data are presented in Table II.

At ppm levels, it is difficult to assess the value of these data. Nevertheless, we were pleased that we recovered the compounds at this level. As seen in Table II, we also recovered benzo-α-anthracene, BAP and coronene in experiments in which we did not add these compounds. Even though we took great care in working with cleaned up materials and experimental chamber, these residues undoubtedly resulted from accidental contamination, i.e., memory effect.

We challenged the POM train with low levels of our test compounds in 8 identical triplicate runs to determine precision. The following comments and conclusions are presented. These data are presented in Table III.

B. Summary of Results

Under identical conditions the average recovery of the PCB and POM materials added ($\times 10^{-4}$) and the standard deviation is as follows:

TABLE II

RECOVERABILITY OF PPM LEVELS OF
BAP, POM AND PCB'S IN EXPERIMENTALLY GENERATED STACK GASES WITH POM TRAINS

Sample	Arochlor 1254	Anthracene	Pyrene	Benz(α)Anthracene	BAP	Coronene
V-II						
WT Added	6.3608 g	-	4.4645 g	-	-	-
Recovered	495 µg	-	478 µg	-	-	-
% x 10^{-4}*	77.8	-	107	-	-	-
W-II						
Added	4.4542 g	2.6026 g	2.7678 g	0.2925 g	0.3091 g	0.1030 g
Recovered	314 µg	27.6 µg	209 µg	15.0 µg	5.6 µg	< 6 µg
% x 10^{-4}*	70.5	10.6	75.5	51.3	18.1	
X-II						
Added	5.2962 g	2.8690 g	3.3669 g	-	-	-
Recovered	299 µg	1.7 µg	83.9 µg	13.8 µg	2.0 µg	4.8 µg
% x 10^{-4}*	56.5	0.6	24.9	-	-	-
Y-II						
Added	7.1170 g	5.0662 g	2.4882 g	-	-	-
Recovered	463 µg	343.2 µg	282.7 µg	32 µg	14.2 µg	-
% x 10^{-4}*	65.1	67.7	113.6	-	-	-
Z-II						
Added	5.8717 g	2.7333 g	2.9706 g	-	-	-
Recovered	529 µg	8.4 µg	217.5 µg	3.2 µg	-	-
% x 10^{-4}*	90.1	3.1	73.2	-	-	-

* Percent recovered.

TABLE II (Continued)

Sample	Arochlor 1254	Anthracene	Pyrene	Benzo(α)Anthracene	BAP	Coronene
A-III						
Added	4.6429 g	1.9286 g	2.2208 g	-	-	-
Recovered	440 μg	114.5 μg	117.0 μg	16.2 μg	-	-
% x 10^{-4}*	94.7	59.4	52.9	-	-	-
B-III						
Added	4.6930 g	3.9826 g	3.7857 g	-	-	-
Recovered	345 μg	-	138.5 μg	6.8 μg	-	-
% X 10^{-4}*	73.6	-	36.6	-	-	-

* Percent recovered.

TABLE III

PRECISION RUNS WITH EIGHT IDENTICAL EXPERIMENTS

Run No.	Percent Recovery ($\times 10^{-4}$)					
	Arochlor 1254	Anthracene	Pyrene	Benz(α)Anthracene	BAP	Coronene
1	85.9	2.2	39.2	-	3.3	-
2	69.5	-	15.6	16.1	-	-
3	55.3	-	41.9	47.5	24.9	-
4	82.4	7.18	44.5	-	-	-
5	116	42.4	144.5	-	-	-
6	68.0	-	1.1	-	-	-
7	81.4	-	-	-	-	-
8	89.6	-	-	-	-	-

	Average Recovery	Standard Deviation $\sigma = \frac{\sqrt{\frac{\Sigma (x - \bar{x})^2}{n-1}}}{\bar{x}} \times 100$
Arochlor 1254	78.4%	48.7%
Anthracene	Data Not Statistically Significant	
Pyrene	64.1%	116%
(High Level)	64.1%	116%
Benz(α)Anthracene (Low Level)	Data Not Statistically Significant	
Benz(α)Pyrene (Low Level)	Data Not Statistically Significant	
Coronene (Low Level)	Data Not Statistically Significant	

C. Conclusions of Laboratory Studies

With identical sampling techniques on many diverse runs, we obtained statistical data to determine precision of recovering the PCB and POM materials at normal and at extremely low levels. It was also our objective to observe and evaluate possible problems encountered in field sampling. Our general conclusions are from an overview of all the laboratory experiments are as follows:

1. Statistically reliable recovery data can be obtained on high level contaminants.

2. These materials can be collected efficiently at low levels, but the precision of sampling is very poor.

3. Recovery is related to the volatility and molecular weight of the particulate being collected.

4. Recovery data on low level contaminants indicated that low level collection and analysis of POM, BAP and PCB's are possible via the procedures developed on this program.

5. Adherence to isokinetic sampling is essential for efficient recoverability because of the varied size distribution of the particulate matter.

6. Even though the test compounds were held at high temperatures in many experiments, a particulate matter cooling effect was observed in the stack which possessed relatively cool walls.

VI. RESULTS FROM PHASE III

The report of results on the laboratory studies on this program is divided into 2 parts, viz., the results of experiments to select the optional sampling train, and the results of experiments to determine the operating characteristics of the selected train.

A. Preliminary Laboratory Test Plan

This laboratory test plan was designed to evaluate the performance of the standard EPA train, a cartridge filter train and a modified version of the Hangerbrauk, Von Lehmden and Mecker train.

A

1. Weigh a known amount of POM and PCB into the sampling nozzles--stainless steel probe at ambient temperature.

2. Pull clean air through the 3 trains for 15 min at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

B

1. Weigh a known amount of POM and PCB into the sampling nozzles--stainless steel probe at ambient temperature.

2. Pull clean air through the 3 trains for 1 hr at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

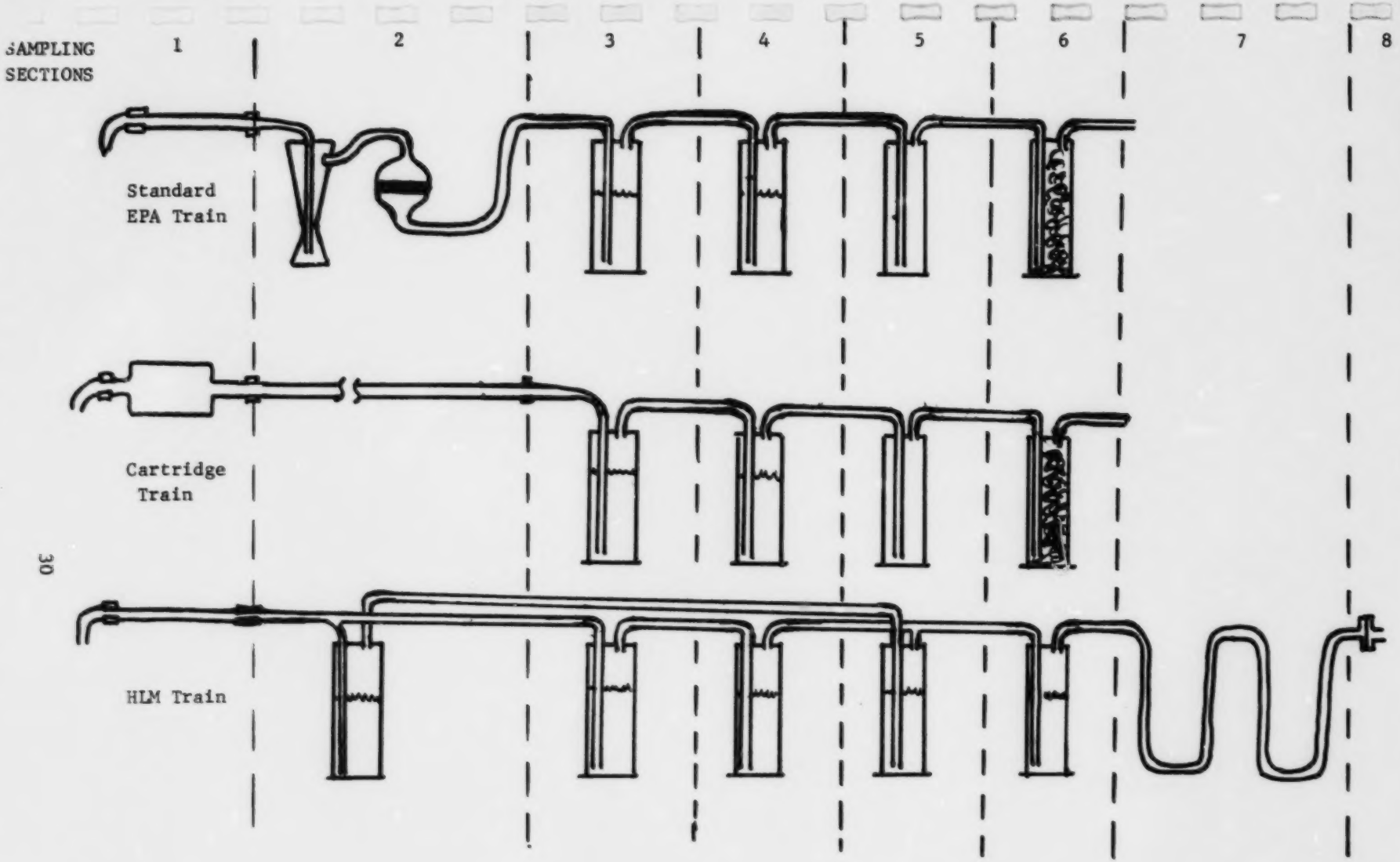


Figure 7 - Selected Stack Sampling Trains
(Sections to be Analyzed for POM and PCB's Are Shown with Dashed Lines)

C

1. Weigh a known amount of POM and PCB into the sampling nozzles--stainless steel probe at ambient temperature.

2. Pull clean air through the 3 trains for 15 min at 4 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

D

1. Weigh a known amount of POM and PCB into the sampling nozzles--stainless steel probe at 300°C.

2. Pull clean air through the 3 trains for 15 min at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

1. Weigh a known amount of POM and PCB into the sampling nozzles--stainless steel probe at 300°C.

2. Pull clean air through the 3 trains for 1 hr at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

1. Weigh a known amount of POM and PCB into the sampling nozzles--stainless steel probe at 300°C.

2. Pull clean air through the 3 trains for 15 min at 4 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

E

1. Weigh a known amount of POM and PCB into the sampling nozzles--with glass probe at ambient temperature.

2. Pull clean air through the 3 trains for 15 min at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

1. Weigh a known amount of POM and PCB into the sampling nozzles--with glass probe at ambient temperature.

2. Pull clean air through the 3 trains for 1 hr at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

1. Weigh a known amount of POM and PCB into the sampling nozzles--with glass probe at ambient temperature.

2. Pull clean air through the 3 trains for 15 min at 4 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

1. Weigh a known amount of POM and PCB into the sampling nozzles--with glass probe at 300°C.

2. Pull clean air through the 3 trains for 15 min at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

1. Weigh a known amount of POM and PCB into the sampling nozzles--with glass probe at 300°C.

2. Pull clean air through the 3 trains for 1 hr at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

1. Weigh a known amount of POM and PCB into the sampling nozzles--with glass probe at 300°C.

2. Pull clean air through the 3 trains for 15 min at 4 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

F

1. Weigh a known amount of POM and PCB into the sampling nozzles--stainless steel probe at ambient temperature.

2. Pull clean air saturated with water through the 3 trains for 1 hr at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

1. Weigh a known amount of POM and PCB into the sampling nozzles--stainless steel probe at 300°C.

2. Pull clean air saturated with water through the 3 trains for 1 hr at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

1. Weigh a known amount of POM and PCB into the sampling nozzles--with glass probe at ambient temperature.

2. Pull clean air saturated with water through the 3 trains for 1 hr at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

1. Weigh a known amount of POM and PCB into the sampling nozzles--with glass probe at 300°C.

2. Pull clean air saturated with water through the 3 trains for 1 hr at 2 cfm.

3. Analyze each of the 8 sections of the train presented in Figure 7.

During the first part of laboratory studies, we completed 21 test runs in triplicate. These test runs were replicated to establish the precision of the test procedures and results. These studies indicated that the precision is $\pm$ 0.4% relative average deviation.

The above test procedures were employed during the initial months of this program to generate the data presented below. These data are the triplicate averages of 21 test runs.

TEST RUN 1

Conditions

Standard EPA Train
Probe and Oven Temperature - Ambient
Carrier - Inert Silica
POM Added:

Anthracene	25.040 mg
Pyrene	26.152 mg
Benz(α)anthracene	24.242 mg
Benz(α)pyrene	24.339 mg
Coronene	14.333 mg

Total Gas Volume - 1.60 m^3 (0.028 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg) Anthracene	Pyrene	BAA	BAP	Coronene
1A	1.655	0.849	3.957	2.813	2.546
2A	17.190	21.680	13.674	15.514	6.854
3A	0.027	0.035	0.056	0.041	-
4A	-	0.029	0.160	-	-
5A	-	-	-	-	-
Total	18.872	22.593	17.847	18.368	9.400
% Recovery	75.37	86.39	73.62	75.47	65.58

TEST RUN 2

Conditions

Standard EPA Train
Oven Temperature - 400°F
Probe Temperature - 600°F
Carrier - Inert Silica
POM Added:

Anthracene	21.269 mg
Pyrene	24.377 mg
Benz(α)anthracene	20.592 mg
Benz(α)pyrene	20.674 mg
Coronene	12.174 mg

Total Gas Volume - 1.40 m^3 (0.028 m^3/min)

Recovery Data (Average Value of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1B	0.790	0.595	1.853	2.302	0.717
2B	12.313	23.105	11.790	12.319	6.831
3B	1.172	0.560	0.325	-	-
4B	0.050	0.074	0.097	-	-
5B	-	-	-	-	-
Total	14.325	24.334	14.065	14.621	7.548
% Recovery	67.35	99.82	68.30	70.72	62.00

TEST RUN 3

Conditions

Standard EPA Train
Oven Temperature - 400°F
Probe Temperature - 600°F
No Carrier
POM Added:

Anthracene	35.822 mg
Pyrene	37.560 mg
Benz(α)anthracene	37.761 mg
Benz(α)pyrene	39.249 mg
Coronene	29.679 mg

Total Gas Volume - 1.26 m^3 (0.028 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1E	2.129	2.566	3.477	4.268	3.714
2E	25.467	25.787	27.484	32.243	20.286
3E	2.274	1.024	1.121	0.259	0.034
4E	0.109	0.144	0.132	-	-
5E	0.030	-	-	-	-
Total	30.010	29.521	32.214	36.770	24.034
% Recovery	83.78	78.60	85.31	93.68	80.98

TEST RUN 4

Conditions

Standard EPA Train
Probe and Oven Temperature - Ambient
Carrier - Fly Ash
POM Added:

Anthracene	6.946 mg
Pyrene	6.803 mg
Benz(α)anthracene	5.871 mg
Benz(α)pyrene	6.178 mg
Coronene	5.419 mg

Total Gas Volume - 0.71 m^3 (0.014 m^3/min)

Recovery Data (Average Value of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1G	3.890	3.701	2.723	3.518	2.611
2G	2.638	1.570	1.218	1.628	1.579
3G	0.103	0.076	0.154	0.100	-
4G	-	-	-	-	-
5G	-	-	-	-	-
Total	6.631	5.347	4.095	5.246	4.190
% Recovery	95.47	78.60	69.75	84.91	77.32

TEST RUN 5

Conditions

Standard EPA Train
Probe Temperature - 600°F
Oven Temperature - 400°F
No Carrier
POM Added:

Anthracene	7.538 mg
Pyrene	8.625 mg
Benz(α)anthracene	7.443 mg
Benz(α)pyrene	7.832 mg
Coronene	6.870 mg

Total Gas Volume - 0.71 m^3 (0.014 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1H	C.535	0.554	1.055	1.340	2.118
2H	6.799	7.381	5.626	6.703	4.181
3H	0.059	0.088	0.089	-	-
4H	-	-	-	-	-
5H	-	-	-	-	-
Total	7.393	8.023	6.770	8.043	6.299
% Recovery	98.08	93.02	90.96	102.69	91.69

TEST RUN 6

Conditions

Cartridge Filter (Carbon) Train
Probe and Oven Temperature - Ambient
Carrier - Inert Silica
POM Added:

Anthracene	24.273 mg
Pyrene	25.351 mg
Benz(α)anthracene	23.500 mg
Benz(α)pyrene	23.594 mg
Coronene	13.894 mg

Total Gas Volume - 1.18 m^3 (0.028 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1C	19.000	25.643	22.563	18.313	9.800
2C	0.016	0.020	0.549	0.168	0.088
3C	-	0.017	0.007	0.036	0.052
4C	-	0.010	0.017	-	-
5C	-	-	-	-	-
Total	19.016	25.690	23.136	18.517	9.940
% Recovery	78.34	101.34	98.45	78.48	71.54

TEST RUN 7

Conditions

Cartridge Filter (Carbon) Train
Oven Temperature - 400°F
Probe and Cartridge Temperature - 600°F
Carrier - Inert Silica
POM Added:

Anthracene	29.868 mg
Pyrene	31.194 mg
Benz(α)anthracene	31.916 mg
Benz(α)pyrene	29.032 mg
Coronene	18.196 mg

Total Gas Volume - 1.16 m^3 (0.028 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1D	26.864	27.214	29.846	24.615	17.903
2D	-	0.040	0.174	0.172	0.276
3D	0.025	0.030	0.160	0.065	-
4D	2.736	1.439	0.619	0.459	-
5D	0.217	0.202	0.547	-	-
Total	29.842	28.926	31.346	25.311	18.179
% Recovery	99.91	92.73	98.21	87.18	99.91

TEST RUN 8

Conditions

HLM Train
Probe and Oven Temperature - Ambient
Carrier - Fly Ash
POM Added:

Anthracene	71.558 mg
Pyrene	70.646 mg
Benz(α)anthracene	61.822 mg
Benz(α)pyrene	64.257 mg
Coronene	48.590 mg

Total Gas Volume - 1.26 m^3 (0.028 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1F	4.236	1.566	4.545	5.693	6.198
2F	21.876	24.746	16.472	15.788	8.854
3F	39.276	42.758	29.561	30.600	22.668
4F	-	-	-	-	-
5F	-	-	-	-	-
Total	65.388	69.070	50.578	52.081	37.720
% Recovery	91.38	97.77	81.81	81.05	77.63

TEST RUN 9

Conditions

Train:	Standard EPA
Probe Temperature:	Ambient
Oven Temperature:	Ambient
Carrier:	None
POM Added:	

Anthracene	85.529 mg
Pyrene	104.249 mg
Benz(α)anthracene	47.847 mg
Benz(α)pyrene	14.831 mg
Coronene	15.743 mg

Total Gas Volume: 1.69 m^3 (0.057 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1K	4.832	8.050	7.025	1.997	1.924
2K	84.324	99.632	38.167	12.120	9.072
3K	0.017	0.033	0.060	0.026	0.104
4K	-	0.028	0.008	-	-
5K	-	-	-	-	-
6K	-	-	-	-	-
Total	89.173	107.743	45.260	14.143	11.100
% Recovery	104.26	103.35	94.59	95.36	70.51

TEST RUN 10

Conditions

Train:	Standard EPA
Probe Temperature:	600°F
Oven Temperature:	400°F
Carrier:	None
Pom Added:	

Anthracene	81.67 mg
Pyrene	99.546 mg
Benz(α)anthracene	45.688 mg
Benz(α)pyrene	14.162 mg
Coronene	15.033 mg

Total Gas Volume: 1.93 m^3 (0.057 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1L	41.184	47.300	19.365	3.073	4.739
2L	29.417	30.251	15.295	4.897	3.264
3L	9.835	12.811	4.948	0.465	0.052
4L	1.505	1.795	0.626	0.038	0.154
5L	0.394	0.411	0.121	0.008	-
6L	-	-	-	-	-
Total	82.335	92.568	40.355	8.480	8.209
% Recovery	100.81	92.99	88.33	59.88	54.61

TEST RUN 11

Conditions

Train:	Cartridge (Charcoal)
Probe Temperature	Ambient
Oven Temperature	Ambient
Carrier:	None
POM Added:	

Anthracene	81.320 mg
Pyrene	99.119 mg
Benz(α)anthracene	45.492 mg
Benz(α)pyrene	14.102 mg
Coronene	14.969 mg

Total Gas Volume: 1.70 m^3 (0.057 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1M	72.028	82.254	32.588	10.383	8.616
2M	2.480	2.831	3.408	0.504	0.254
3M	1.206	1.679	0.866	0.083	0.056
4M	0.540	0.728	0.274	0.028	0.021
5M	0.385	0.506	0.161	0.018	-
6M	-	-	-	-	-
Total	76.639	87.998	37.297	11.016	8.947
% Recovery	94.24	88.78	81.99	78.12	59.77

TEST RUN 12

Conditions

Train:	Cartridge (Alumina)
Probe Temperature:	Ambient
Oven Temperature:	Ambient
Carrier:	None
POM Added:	

Anthracene	83.329 mg
Pyrene	101.567 mg
Benz(α)anthracene	46.616 mg
Benz(α)pyrene	14.450 mg
Coronene	15.338 mg

Total Gas Volume: 1.75 m^3 (0.057 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1N	78.867	93.132	40.149	12.687	9.982
2N	1.113	0.446	0.374	0.088	0.533
3N	0.175	0.148	0.075	-	0.365
4N	0.128	0.148	0.055	-	-
5N	0.007	0.029	0.012	-	-
6N	-	-	-	-	-
Total	80.290	93.903	40.665	12.775	10.880
% Recovery	96.35	92.45	87.23	88.41	70.93

TEST RUN 13

Conditions

Train:	Cartridge (Charcoal)
Probe Temperature:	600°F
Oven Temperature:	400°F
Carrier:	None
POM Added:	

Anthracene	83.105 mg
Pyrene	101.130 mg
Benz(α)anthracene	46.491 mg
Benz(α)pyrene	14.411 mg
Coronene	15.297 mg

Total Gas Volume: 1.78 m^3 (0.057 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1Ø	66.500	74.742	33.080	5.438	5.811
2Ø	-	0.015	0.018	0.014	0.122
3Ø	2.158	1.563	0.596	0.075	-
4Ø	0.533	0.707	0.159	0.036	-
5Ø	0.071	0.082	0.016	-	-
6Ø	-	-	-	-	-
Total	69.262	77.109	33.869	5.563	5.933
% Recovery	83.34	76.25	72.85	38.60	38.79

TEST RUN 14

Conditions

Train:	Cartridge (Alumina)
Probe Temperature:	600°F
Oven Temperature:	400°F
Carrier:	None
POM Added:	

Anthracene	87.283 mg
Pyrene	106.387 mg
Benz(α)anthracene	48.828 mg
Benz(α)pyrene	15.136 mg
Coronene	16.066 mg

Total Gas Volume: 1.70 m^3 (0.057 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1P	74.025	76.183	33.428	9.348	4.785
2P	-	0.026	0.027	-	0.111
3P	2.961	2.567	0.325	0.034	0.149
4P	2.382	2.066	0.159	0.030	-
5P	0.354	0.321	0.024	-	-
6P	-	-	-	-	-
Total	79.722	81.163	33.963	9.411	5.045
% Recovery	91.34	76.29	69.56	62.18	31.40

TEST RUN 15

Conditions

Train:	Cartridge (Alumina)
Probe Temperature:	Ambient
Oven Temperature:	Ambient
Carrier:	None
POM Added:	

Anthracene	84.509 mg
Pyrene	103.006 mg
Benz(α)anthracene	47.276 mg
Benz(α)pyrene	14.655 mg
Coronene	15.556 mg

Total Gas Volume: 0.85 m^3 (0.014 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1Q	85.428	102.105	42.740	13.376	9.222
2Q	-	0.025	0.011	-	0.082
3Q	0.314	0.293	0.168	0.028	-
4Q	0.093	0.109	0.132	-	-
5Q	0.017	0.027	0.012	-	-
6Q	-	-	-	-	-
Total	85.852	102.558	43.062	13.404	9.304
% Recovery	101.59	99.57	91.09	91.46	59.81

TEST RUN 16

Conditions

Train:	Cartridge (Alumina)
Probe Temperature:	Ambient
Oven Temperature:	Ambient
Carrier:	None
POM Added:	

Anthracene	87.889 mg
Pyrene	107.126 mg
Benz(α)anthracene	49.167 mg
Benz(α)pyrene	15.241 mg
Coronene	16.178 mg

Total Gas Volume: 1.59 m^3 (0.028 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1R	70.405	79.534	35.923	11.012	6.932
2R	0.020	0.041	0.664	-	0.151
3R	0.037	0.020	0.022	-	0.138
4R	-	0.032	-	-	-
5R	-	-	-	-	-
6R	-	-	-	-	-
Total	70.462	79.627	36.609	11.012	7.221
% Recovery	80.17	74.33	74.46	72.25	44.63

TEST RUN 17

Conditions

Train:	Cartridge (Alumina)
Probe Temperature:	600°F
Oven Temperature:	400°F
Carrier:	None
POM Added:	

Anthracene	83.297 mg
Pyrene	101.528 mg
Benz(α)anthracene	46.598 mg
Benz(α)pyrene	14.444 mg
Coronene	15.332 mg

Total Gas Volume: 0.85 m^3 (0.014 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1S	50.960	57.900	27.772	7.598	7.969
2S	0.033	1.029	1.450	0.072	-
3S	13.067	13.613	1.613	0.163	-
4S	0.564	0.865	0.144	-	-
5S	0.058	0.061	0.020	-	-
6S	-	-	-	-	-
Total	64.682	73.468	30.999	7.833	7.969
% Recovery	77.65	72.36	66.52	54.23	51.98

TEST RUN 18

Conditions

Train:	Cartridge (Alumina)
Probe Temperature:	600°F
Oven Temperature:	400°F
Carrier:	None
POM Added:	

Anthracene	81.351 mg
Pyrene	99.157 mg
Benz(α)anthracene	45.510 mg
Benz(α)pyrene	14.107 mg
Coronene	14.974 mg

Total Gas Volume: 1.70 m^3 (0.028 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1T	71.419	84.634	40.521	11.799	5.466
2T	-	0.009	0.038	0.017	0.092
3T	2.350	5.700	1.957	0.120	0.037
4T	1.636	3.327	0.568	-	-
5T	0.416	0.662	0.168	-	-
6T	-	-	-	-	-
Total	75.821	94.332	43.252	11.936	5.595
% Recovery	93.20	95.13	95.04	84.61	37.36

TEST RUN 19

Conditions

Train:	Cartridge (Diatomaceous Earth)
Probe Temperature:	Ambient
Oven Temperature:	Ambient
Carrier:	None
POM Added:	

Anthracene	82.404 mg
Pyrene	99.157 mg
Benz(α)anthracene	46.099 mg
Benz(α)pyrene	14.290 mg
Coronene	15.168 mg

Total Gas Volume: 0.85 m^3 (0.014 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1U	82.900	102.580	45.305	14.478	4.206
2U	-	0.027	0.461	0.025	-
3U	0.064	0.146	0.111	-	0.153
4U	-	0.044	0.072	-	-
5U	-	0.008	0.025	-	-
6U	-	-	-	-	-
Total	82.964	102.805	45.973	14.503	4.359
% Recovery	100.68	103.68	99.73	101.49	28.74

TEST RUN 20

Conditions

Train:	Cartridge (Diatomaceous Earth)
Probe Temperature:	Ambient
Oven Temperature:	Ambient
Carrier:	None
POM Added:	

Anthracene	70.222 mg
Pyrene	85.592 mg
Benz(α)anthracene	39.284 mg
Benz(α)pyrene	12.177 mg
Coronene	12.926 mg

Total Gas Volume: 1.76 m^3 (0.028 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg)				
	Anthracene	Pyrene	BAA	BAP	Coronene
1V	49.102	58.050	27.063	8.343	8.114
2V	0.007	0.058	0.242	0.025	0.031
3V	0.032	0.039	0.104	-	-
4V	0.018	0.059	0.117	-	-
5V	0.011	0.018	0.029	-	-
6V	-	-	-	-	-
Total	49.169	58.225	27.555	8.368	8.145
% Recovery	70.02	68.03	70.14	68.72	63.01

TEST RUN 21

Conditions

Train:	Cartridge (Diatomaceous Earth)
Probe Temperature:	Ambient
Oven Temperature:	Ambient
Carrier:	None
POM Added:	

Anthracene	81.742 mg
Pyrene	83.575 mg
Benz(α)anthracene	74.336 mg
Benz (α)pyrene	-
Coronene	12.178 mg

Total Gas Volume: 1.70 m^3 (0.057 m^3/min)

Recovery Data (Average Values of Triplicate Experiments)

Sample Location	POM Recovered (mg) Anthracene	Pyrene	BAA	BAP	Coronene
1W	59.147	58.016	56.152	NOT ANALYZED YET	
2W	0.010	0.048	0.114		
3W	0.053	0.029	0.094		
4W	0.029	0.073	0.097		
5W	0.024	0.047	0.193		
6W	-	-	-		
Total	59.263	58.213	56.649		
% Recovery	72.50	69.65	76.20		

B. Trends in the Selection Experiments

The trends in the data from our laboratory studies are presented below:

1. Recovery of POM, as may be expected, is more efficient when large amounts of POM were employed than when lesser amounts are employed.

2. The POM material is isolated further along the EPA and HLM trains and with better efficiency when the probe and oven are heated to temperatures higher than 300°C. This fact is especially true for the more volatile and lighter POM.

3. Recovery of the test compounds in the cartridge materials was relatively inefficient compared to the EPA and modified HLM train.

4. Recovery appears to be more efficient in all trains at the lower flow rates. The loss of sorbents from the impingers is also minimized because the condensation efficiency of the train is increased by the slower gas flow rates.

5. In both the cartridge train and EPA train the recovery efficiency appears to be highly dependent upon the ability of the cartridge to adsorb and filter, and the ability of the cyclone and filtering assembly to physically remove the POM material from the passing gases, respectively. Chemisorption does not appear to be prevalent. Consequently, a consistent percent of the POM collected (that which does not readily pass through the trains) can be recovered easily.

6. Collection errors seem to lie most heavily in the ability of the analyst to quantitatively remove the particulate matter after a run. However, this error in collection is constant and predictable.

7. For particulate collection and extraction, the EPA train seems to be the most convenient and easiest train with which to work. Therefore, the HLM train was modified to resemble (physically) the EPA train.

8. In the presence of the large amounts of particulate matter and moisture, a clogging problem appears to develop in the cartridge train.

C. Selection of One Train

After selecting the 3 trains for the laboratory studies, the primary objective of the laboratory studies was to systematically challenge

the features of all the trains in combination for the development of one highly efficient train that would be convenient to use in stationary source sampling programs. This phase of our laboratory studies was successfully completed by selecting a modified version of the HLM train for the remainder of the evaluations. Later we named this train the POM train.

A general evaluation of the 3 trains is presented. This evaluation is an overview of the results generated during the first 3 months of laboratory effort and the field study during the fourth month.

1. The EPA Train

The EPA train performs quite efficiently at low flow rates and temperatures. At higher flow rates and temperatures or when it is operated for long periods, its efficiency drops dramatically. This train is the easiest to use and has the best precision on repetitive runs. However, the heavy POM are not recovered from this train efficiently as light POM and PCB. Thus, distorted results are inevitable.

2. The HLM Train

The HLM train possesses the best average percent recovery under all test conditions. Temperature, gas flow rate, type of probe material and other variables have less effect on PCB and POM recoverability than the other trains. This train can be operated at high flow rates and temperatures for long periods to collect the large samples required for analyzing low levels of PCB and POM. It also has the advantage of collecting all the PCB and POM materials at about the same efficiency. However, this train has 3 disadvantages. It is delicate, cumbersome, and the precision in replicate runs is much poorer than the other trains. These disadvantages are caused by manipulating its relatively large number of components. Later in the program these disadvantages were overcome by modifying this train.

3. The Cartridge Train

The cartridge train is the least effective train. Changes in temperature, flow rate and other variables are much more pronounced, and the PCB's and lighter POM are recovered to a much greater extent then the heavier POM. A part of this problem results from the fact that the heavier POM are irreversibly sorbed to the sorbent in the cartridge and in the silica gel at the end of the train. As with the HLM train, this system is also cumbersome. When carbon is employed as the sorbent and the system is operated at low temperatures and flow rates for short periods, this train is more effective than the others.

4. Overall Percent Recovery

We critically reviewed the results from the Laboratory Test Plan in this program. Even though other tests could have been conducted according to this Plan, the 77 test sampling runs (42 runs) provided sufficient data to justify the selection of the modified HLM train, i.e., the POM train.

The key to this justification is the percent recovery of BAP, PCB and other POM. Implicit in this term is the efficiency of collection, amount of degradation and reactivity of the POM, the degree of tenacity that the POM are held in the trains, and statistical errors in manipulating the samples.

The average percent recovery of BAP, PCB's and other POM under all test conditions in 77 test sampling runs are summarized as follows:

HLM Sampling Train	92.25%
Standard EPA Train	83.99%
Cartridge Train	74.88%

The variables studied in the Laboratory Test Plan include: temperature; moisture content of gases; flow rate of gases through the trains; probe-liner materials; reactivity and volatility of BAP, PCB's and other POM in the trains; components of the sampling systems; nature of the liquid in the bubblers and impingers; type of sorbents in the cartridge; concentration of the BAP, PCB and other POM passed into the trains; and concentration of adulterants in the "stack" gases.

D. Temperature

In our laboratory studies, we held the temperature of the "stack" gases and the probe at ambient (23°C) or at high (300°C) temperatures. The effect of temperature on the recovery of the BAP, PCB and other POM with other variables constant are as follows:

Train	Temperature	% Recovery	% Difference
HLM	Ambient	95.50	3.36
	High	92.14	
EPA	Ambient	87.49	6.30
	High	81.19	
Cartridge	Ambient	79.38	9.01
	High	70.37	

The positive differences in the percent recovery between ambient and high temperatures for each train indicate that an overall reduction in the collection efficiency is experienced at the higher temperature and that this trend continues at even higher temperatures. However, upon examination of the recoverability of specific POM in these studies, this trend is not valid for PCB, pyrene and anthracene. These compounds are recovered completely at all temperatures, but in components further down stream in the train. The major factor in the decrease in the overall recovery of POM at higher temperatures is that benzo(α)anthracene (BAA), benzo(α)pyrene (BAP), and coronene (COR) are partially swept out of the train. These compounds partially pass through the trains because they do not interact with the solvents in the impingers. Also, we have shown that the vaporized solvents carry BAA, BAP and COR out of the train even though precautions are taken to maintain these solvents at 0°C.

It is important to emphasize here that the POM compounds that pass out of the EPA and cartridge trains are probably trapped in the silica gel. Thus, even though the POM was probably efficiently collected in these trains, it could not be removed from this tenacious sorbent.

It is also important to note that the volatility of the solvents in the impingers of the sampling trains on conventional stack sampling programs is not an important consideration because lower flow rates and shorter sampling periods are usually required. Because POM occurs at low levels, as demonstrated in one field study, flow rates of at least 1 cfm for at least 8 hr (480 cu ft) will be required in future field studies to obtain a convenient analytical sample.

E. Flow Rates

With all other variables constant, we found that the percent recovery of POM was greater at the lower (0.057 m^3/min) than at the higher (0.113 m^3/min) flow rates:

Train	Flow Rate	% Recovery	% Difference
HLM	Low	92.36	0.22
	High	92.14	
EPA	Low	87.39	17.12
	High	70.27	
Cartridge	Low	76.87	2.66
	High	74.21	

As in our studies with only temperature as a variable, these differences in collection efficiency indicate that the HLM train provides the best physical barrier with the ancillary benefit of preventing the solvent from vaporizing from the train.

Again note that the low results in the experiments with flow rate as the only variable using the EPA and cartridge trains do not necessarily reflect inefficient collection. The recovery data is lower than those of the HLM train because BAA, BAP and COR cannot be completely extracted from the sorbents in the cartridge or from the silica gel at the end of the train. Activated carbon irreversibly sorbs these 3 compounds. Nevertheless, activated carbon is the best overall sorbent for PCB and POM:

Sorbent	Apparent % Recovery
Activated Carbon	80.94
Alumina	76.12
Kieselguhr	69.59

Thus, the tests where only temperature or gas flow rate are varied, the EPA and cartridge trains provide the least physical barrier to the test compounds because they have fewer components than the HLM train. Concomitantly, they have a lower pressure drop in the system.

F. Stability of POM

Another important consideration in the selection of the "best" train was the stability of the PCB and POM within the train. The degree of degradation and reactivity of these materials does not appear to cause a variance in the data in any of the trains. If the collected samples are not analyzed immediately after collection, error due to degradation or reactions is considerable, especially if the samples are held for more than 1 day. Additional peaks are readily observed on our gas chromatograms with retention times between anthracene and BAP and at retention times longer than coronene. These peaks appear even when great care is taken to preclude oxygen and light below 550 nm from the trains, analytical vessels and storage containers.

G. Adulterant Gases

Gases, such as HCl, SO_x, NO_x, O_2, CO and H_2O have a profound effect on the recoverability of POM but not PCB's. Although it is reasonably certain that these gases react with the POM in the gas phase,

especially with high gas temperatures, we have not discounted the possibility of reactions occurring in the impingers. In any case, significant differences were not observed in performance of the 3 trains.

H. Physical Sorption

To determine if physical sorption sites of the probe liner were prevalent, a series of test runs were conducted with probes made of Vycor and stainless steel. The results of this study, with other variables constant, are summarized below.

Train	Probe Liner	% Recovery	% Difference
HLM	Vycor	90.52	- 2.76
	Stainless	93.28	
EPA	Vycor	86.54	2.55
	Stainless	83.99	
Cartridge	Vycor	74.85	- 0.06
	Stainless	74.91	

Relatively small amounts of PCB, anthracene and pyrene were found within the probe in these studies, especially when the probe and entering gases were heated to 300°C. Larger amounts of the heavier POM, *viz.*, benz(α)anthracene, benz(α)pyrene and coronene, were recovered from the probes in all experiments. In experiments that were conducted at 23°C and at a flow rate of 1.057 m^3/min or less, all POM was consistently collected in the stainless steel probe, but not to the same extent in the Vycor probe. Undoubtedly, the rougher surface of the stainless steel provides greater physical barrier to flow than Vycor, but this is not an important factor. The materials are recovered from both liners quite readily.

I. Chemical Reactivity in the Probe

More importantly, we were concerned about the chemical reactivity or catalytic effects of the probe materials. Even when we deliberately established conditions that were conducive to chemical reactions, we did not observe a difference in reactivity or catalytic effects between Vycor and stainless steel. It is now our opinion that either material may be used as a probe liner without concern for physical or chemical interactions. Nevertheless, if a choice must be made, we would select Vycor because less POM is physically entrained.

J. General Evaluations of the Modified HLM Train

One of the more important tasks which we performed during this program was to evaluate the efficiency of the modified HLM train under a wide variety of conditions. We varied temperature, gas flow rate, moisture content, concentration of fly ash, NO_x, SO_x, and hydrocarbons, and the type of absorbing solvents contained in the impingers.

The average simultaneous recovery under all conditions was:

POM = 92%
PCB = 81%

Of the above variables, only the addition of large amounts of steam to the simulated stack gases had a pronounced effect on the collection efficiency of the HLM train. For the first time, 100% of the POM and PCB generated in our test unit was collected in the train. Thus, the presence of moisture-laden gases has a beneficial effect on collection efficiency. Another, perhaps related beneficial effect of high moisture was that very little POM and PCB were collected in the probe. Essentially, all of these materials were absorbed in the fly ash or in the impingers. Although 3 phases appeared in the impingers when non-polar organic solvents were used, the presence of these phases did not detract from the ease of recovery or collection efficiency. The only detrimental effect of the high moisture content was the relatively large volume of water that was condensed in the system. However, this effect was merely a matter of inconvenience.

K. Selection of a Solvent for the HLM Train

The objective of this task was to determine the most suitable solvent for collecting POM and PCB's in the POM train. We selected several solvents including butanol, benzene, water, toluene and xylene. A summary of these studies is presented below:

Solvent	Stack Gas Temperature, °C	Collection Efficiency POM	PCB
Butanol	350	87	67
	23	93	72
Benzene	350	93	79
	23	-	-
Water	350	70	69
	23	83	68
Toluene	350	98	81
	23	99	83
Xylene	350	89	81
	23	95	85

To obtain the above collection efficiency data, the modified HLM train was operated at either 23°C or 350°C with a gas flow rate through the system of 0.085 m^3/min for 3 hr. Fly ash was continuously added to the stack gases throughout these experiments to simulate real stack conditions.

We observed that water, which is the absorbent used in the publications describing the original HLM train, sorbs the POM and PCB's least efficiently while toluene and xylene sorb these test materials most efficiently. From the above data it would appear that toluene should be the solvent of choice. However, this is not the case. Toluene has the disadvantages of producing noxious vapors, and it volatilizes readily even in an ice bath. Thus, we have selected xylene as the absorbing solvent for future evaluations. It does not have the disadvantages of toluene and collects POM nearly as well and PCB's better than toluene.

L. Interaction of Fly Ash with POM and PCB

It is not known if POM and PCB's are carried on or within fly ash or if the POM and PCB's occur in the free state in real stack gases. We believe it is a combination of these situations. Nevertheless, it is highly important to know how POM and PCB's are transported in stack gases because the size of the particulate matter and the tenacity of fly ash for POM and PCB have a profound influence on collection efficiency.

In attempting to answer these questions during the program, we simulated as closely as possible the conditions that exist in a real stack. We first generated fly ash only and analyzed the collected material for POM and PCB's. None was found. Then we generated the fly ash in the presence of POM and PCB's under the same conditions. We found that the fly ash does not degrade or in any manner alter the POM and PCB's. However, about 90% of the collected POM and PCB's were adsorbed in or on the fly ash. The other 10% was collected in the impinger solutions.

We also generated the POM and PCB's under the above conditions in the absence of fly ash. The efficiency of collection of the POM and PCB's was nearly 10% less than in the above experiments. Thus, it is certain that the fly ash aids in the physical removal of the POM and PCB's from the stack gases.

Based on the results of these experiments, we decided to make another modification of the HLM train. This train consisted of a glass-lined probe, a cyclone or glass fiber filter, the impingers of the HLM train and controls of the standard EPA train. This train recovered the POM and PCB's more efficiently than any of the other trains that we have studied

previously, and it therefore improved the potential for convenient use in the field. By merely changing the manifold in the standard EPA train and adding one additional bubbler half-filled with silica gel at the end of the train, a very compact, rugged train can be fabricated.

As a continuation of these laboratory experiments we studied a great variety of solvents for use in the impinger train. The results of this study during this report period confirmed preliminary indications that xylene collected both POM and PCB's more efficiently; the collection efficiencies are 95% and 85%, respectively.

From these data, we designed and fabricated the POM train into a unit that is convenient to use in field surveys. This arrangement of impingers and other glassware, as shown in the schematic drawing in Figure 8, is compatible with existing stack sampling equipment sold by Western Precipitation and Research Appliance Company.* Modifications of the ovens and the impinger-cooling chambers of the units sold by these companies are not required. To convert these standard EPA trains to the modified HLM train, we merely fabricated four new glass connectors, and added one bubbler. We retained all conventional U-tube connectors.

Simultaneously, we determined that a fiberglass filter is not needed in the POM system if a cyclone is used. In fact, the system appears to operate more efficiently and accurately when the filter is not inserted into the train. The reasons for this fact are: (1) less analytical handling because of fewer components; and (2) the flow tendency to clog during long survey inventories of stacks which have high particulate loading.

M. POM Stability Studies

To determine the stability of POM after collection, we analyzed the total particulate matter collected from stack inventories immediately and again after 3 months. These samples were stored at room temperature in clear bottles and deliberately exposed to air. In this experiment, degradation of the POM materials was seen via gas chromatography at a level of 0.122 mg. Gas chromatographic peaks between anthracene and pyrene were observed after this 3-month storage. The initial and final values determined for the POM were the following:

* Mention of trade name or commercial product does not constitute endorsement or recommendations by EPA.

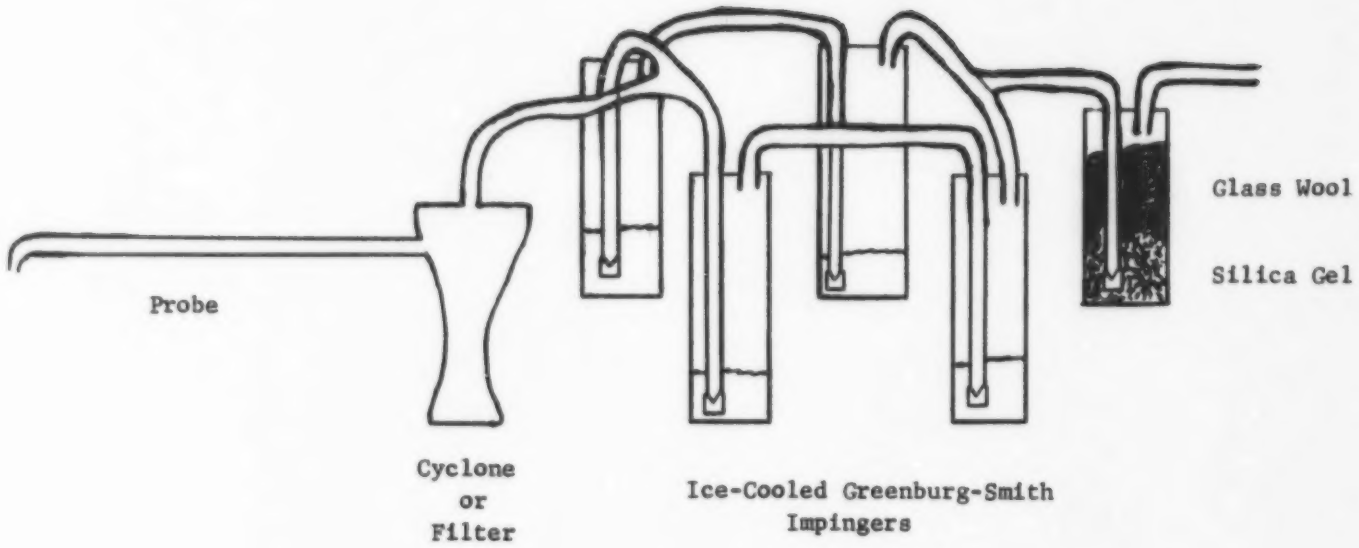


Figure 8 - Schematic Drawing of the Modified HLM Train Packaged in Conventional Equipment

	Initial	Final
Anthracene	71.4 mg	71.3 mg
Pyrene	84.6 mg	84.6 mg
BAA	40.5 mg	40.3 mg
BAP	11.8 mg	11.8 mg
Coronene	5.5 mg	5.6 mg

Thus, even though degradation was observed in this study, it did not appear to be significant. The above POM amounts remained essentially the same.

Another set of samples were stored in the dark, in amber bottles and not exposed to air. The above degradation peaks were not observed in these samples and no significant loss was observed. We conclude from these experiments that POM may be casually stored for at least 3 months without significant effects on the results.

N. Effects on Efficiency of Collection by Varying the Stack Gas Matrices

Eight different stack matrices were ignited and passed through the reaction chamber to the stack in which the POM train was attached. The reaction chamber and stack with pertinent ancillary equipment is presented in Figure 9. The results of these experiments are summarized below:

Carrier Material	Pyrene, µg		Arochlor 1254, µg		Other POM	
	Expected	Obtained	Expected	Obtained	Expected	Obtained
Fly Ash	500	466	200	51	0	819
Polystyrene	0	0	0	0	1,000	3,082
Paper	0	0	2,000	1,342	0	-
Benzene	2,000	211	2,000	270	6,000	683
Rubber	500	325	400	383	0	180
Motor Oil	500	521	400	314	300	207
Grain	500	396	400	151	0	95
Polypropylene	500	191	400	194	0	579

The other POM consisted of benzo(α)anthracene, benzo(α)pyrene and other POM which were not identified. The carrier designated "benzene" is a suspension of known amounts of POM and PCB's in benzene and aerosolized with the ERC generator. The reason for the large deviation from expected levels is that a "large particle scavenger" was inadvertently left in the generator during the run. Thus, these data represent only those materials that have a particle size less than 5 µm.

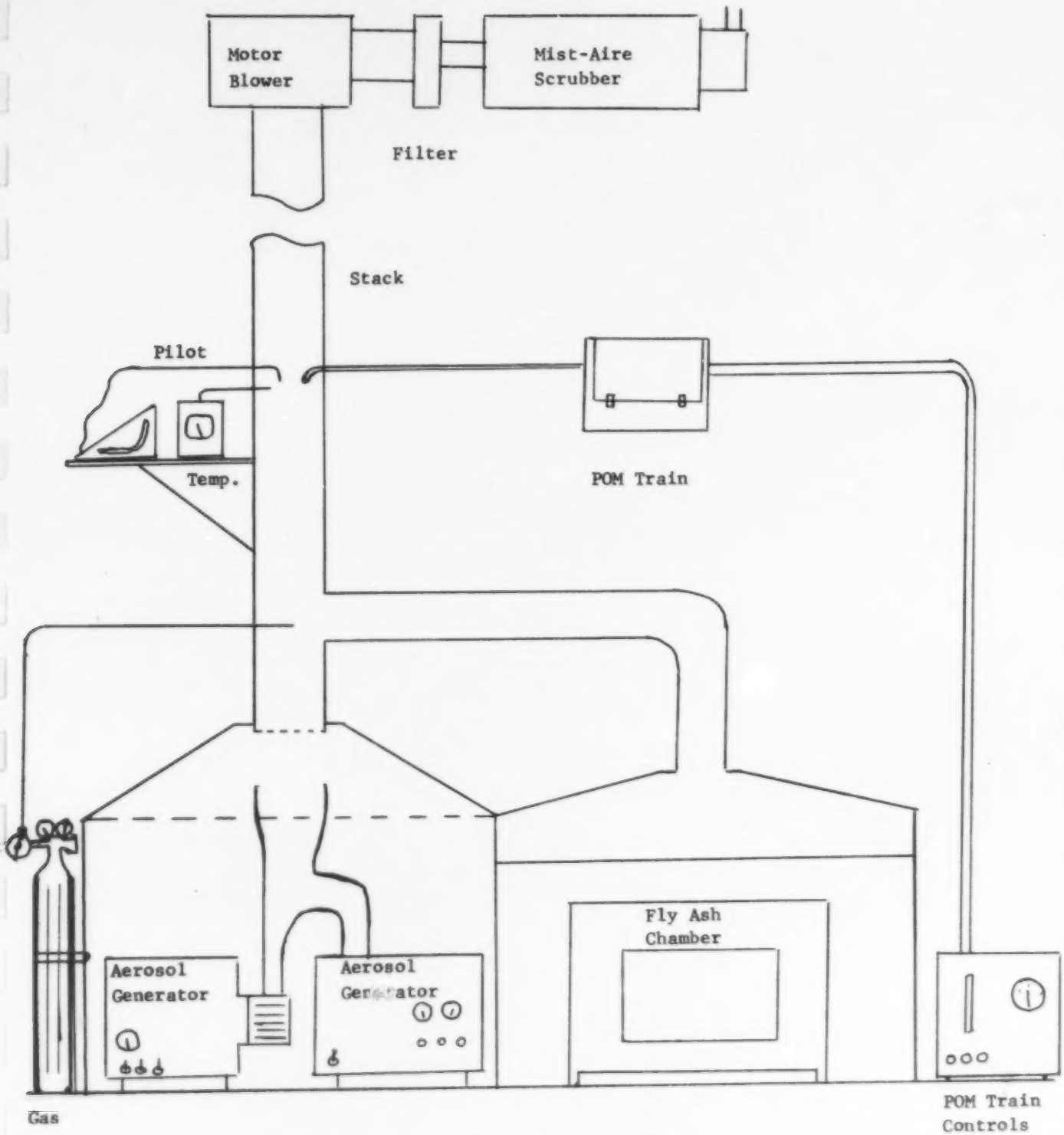


Figure 9 - Laboratory Test Chamber

VII. RESULTS OF FIELD STUDIES

This section of the report provides a general description of each 6 field studies, their objectives, the methods used for collecting the stack gas samples, the analytical methods, results and conclusions. A summary of these field studies is presented in Table IV.

A. Field Study No. 1

The first field inventory was designed to evaluate the 3 sampling trains used in our laboratory studies on a Type I-II high temperature commercial incinerator for POM under identical conditions.

1. Summary of Test Conditions

When the refuse incinerator was charged with cardboard boxes, wood, plastics and other similar refuse at an estimated rate of 575 lb per hr, the emission rate as determined by tests described in the Federal Register was 0.0336 g/m^3 (corrected to 12% CO_2). This value is an average of two runs: 0.035.1 and 0.032.3 g/m^3 (corrected to 12% CO_2).

The hydrocarbon emission rate was determined to be 0.083 lb/day. This emission rate was purposely set below the maximum allowable of 15 lb/day, as set forth in Rule 66 of the Los Angeles County Air Pollution Control District, so we could determine the efficiency of collection of POM on each of the trains under "normal" operating conditions.

2. Sample Treatment After Collection

The total particulate matter collected from this incinerator was collected with our modified POM train, EPA train and cartridge train. The collected materials were treated as follows:

a. The physically-collected particulate matter from each train was submerged in 20 ml of pesticide quality toluene.

b. This mixture was placed in a sonic bath for 1 hr.

c. The residue was filtered and rinsed with 2 5-ml portions of toluene.

d. The filtrate which was mixed with the impinger solutions and train rinsings was evaporated to dryness.

TABLE V

SUMMARY OF FIELD STUDIES

Field Study	Type of Source	Material Burned	Used in Study	Class of Compounds Sought
1	Type I-II High Temperature Incinerator	Refuse	Modified POM Method 5 EPA Cartridge Filter	POM
2	Coal-Burning Steam Generator Plant	Coal	Method 5 EPA Modified POM	POM
3	Copper Reclaiming Incinerator	Wire Insulation Trash	Modified POM	POM, PCB
4	Copper Reclaiming Incinerator	PVC Rubber Tires	Modified POM	POM, PCB
5	Kansas City Missouri Municipal Incinerator	Sludge Trash	Modified POM	POM, PCB
6	Charcoal Burning Restaurant	Grease Wood Charcoal	Modified POM	POM, PCB

e. This residue was taken up to 0.2 m. of toluene

f. Two microliters of these extracts were injected into a Perkin-Elmer Model 900 Gas Chromatograph under the conditions established in our laboratory for POM.

g. The compounds separated on the chromatographic column and represented as peaks were identified by injections of known standard compounds.

h. The peaks identified as POM were quantitated with our POM standards.

3. Results

Based on the fluorescence of the components separated on thin-layer chromatograms and gas chromatographic analyses, we found 1.4 μg of POM material per 1.95 m^3 of stack gas with the EPA Method 5 train.

By comparing the retention times of known compounds to the peaks produced by gas chromatographic analyses of the samples, 7 of the 10 compounds identified were POM that possessed 4-membered rings. The major component in this category was benz(α)anthracene. Three compounds were identified as being 5-membered rings or greater. One of these compounds was identified as benz(α)pyrene.

No other compounds could be identified. The other two trains, the cartridge and HLM train, were found to be much too inconvenient to manipulate on this test and could not be used to collect POM under real field conditions.

B. Field Study No. 2

For the second field inventory, we selected a coal-burning steam generator power plant to evaluate only a modified version of the POM sampling train developed in our laboratory studies for POM. During these studies, we employed a fiberglass bell filter without a cyclone in the train. We also used the Lundgren Impactor to determine particle size distribution of the particulate matter in the stack.

The emission rate as determined by tests described in the Federal Register was 22.22 g/m^3 (corrected to 12% CO_2). This value is an average of two runs: 21.48 and 22.95 g/m^3 (corrected to 12% CO_2).

The emission rate was well above the maximum allowable value of 0.45 g/m^3 (corrected to 12% CO_2) as set forth in Section 18.90 of the Air Pollution Control Ordinance of Kansas City, Missouri. Contrary to the first field test, we selected a stationary source that was emitting greater than allowed particulate matter levels to challenge the modified version of the POM train to determine its capacity to collect large amounts of POM.

1. Sample Treatment

The total particulate matter collected in the train at the Power Generator Plant was collected and treated as follows:

a. The particulate matter physically entrained in the probe and on the filter were collected in pesticide quality toluene.

b. This mixture was placed in a sonic bath for 1 hr.

c. The residue was filtered and rinsed with 2 5-ml portions of toluene.

d. This filtrate and the impinger solutions were evaporated to dryness on a rotary evaporator.

e. The residue from these treatments were taken up in 0.2 ml of toluene.

f. Two microliters of extract were injected into a Perkin-Elmer Model 900 Gas Chromatograph under the conditions established in our laboratory for POM.

g. The compounds were identified by comparing their retention times with that of known compounds.

h. The compounds were quantitated with POM standards.

2. Summary of Results

Particle Size Distribution - Lundgren Impactor

	Particle Size	% Distribution
Stage 1	10 μ or greater	26.67
Stage 2	3 - 10 μ	47.72
Stage 3	1 - 3 μ	7.46
Stage 4	0.3 - 1 μ	1.06
Filter	0.3 μ	17.09

POM Collected on Particulate Matter

First Run: In this run, 51.952 g of particulate matter were collected as 3.83 m^3 of stack air was drawn through the train. The following POM were identified:

26.96 $\mu g/m^3$ Anthracene

6.08 $\mu g/m^3$ Pyrene

7.53 $\mu g/m^3$ Benz(α)Anthracene

The total POM collected in this run was 49.08 $\mu g/m^3$.

Second Run: In this run, 58.453 g of particulate matter were collected as 4.02 m^3 of stack air was drawn through the train. The following POM were identified:

0.64 $\mu g/m^3$ Pyrene

4.98 $\mu g/m^3$ Anthracene

The total POM collected in this run was 14.84 $\mu g/m^3$.

A detailed list of the gas chromatographic data of the two survey runs at the power plant is presented in Table V. We do not know the reason for the difference in the results in what appeared to be two identical experiments.

C. Field Studies Nos. 3 and 4

For our third and fourth field inventories we completed 4 independent field sampling experiments on a copper reclaiming incinerator for both POM and PCB's with the POM sampling train developed in our laboratory studies. During these studies, we employed a fiberglass bell filter without a cyclone in the train. Our objective was to determine POM and PCB's simultaneously under two different field conditions.

The emission rate of this unit as determined by standard recommended inventory tests was 0.76 $\mu g/m^3$ (corrected to 12% CO_2). This value is an average of 4 runs: 0.24 g/m^3 and 1.28 g/m^3 (corrected to 12% CO_2). In the first two runs, 6.190 mg of POM and 1.4 μg of PCB's, were found; and 254 μg of POM and 2.7 μg of PCB's were found in the second two runs.

TABLE V

GAS CHROMATOGRAPHIC DATA ON THE PARTICULATE MATTER COLLECTED ON TWO RUNS AT THE POWER GENERATING PLANT

First Run - 7.33696 Grams

Retention Times	Micrograms	PPM of Dust	Identification
1.25	14.57	1.986	Anthracene
1.50	2.14	0.292	*
2.25	0.22	0.030	*
2.40	0.22	0.030	*
2.80	3.28	0.447	Pyrene
3.5	0.16	0.022	*
4.05	0.19	0.026	*
5.45	4.05	0.552	Benz(α)Anthracene
7.25	1.69	0.230	*
Total	26.53	3.615	

Second Run - 12.02757 Grams

Retention Times	Micrograms	PPM of Dust	Identification
2.3	0.82	0.068	*
2.8	0.52	0.043	Pyrene
3.55	0.52	0.043	*
4.05	0.39	0.032	*
4.55	0.82	0.068	*
5.4	4.14	0.344	Benz(α)Anthracene
6.2	0.31	0.026	*
7.4	4.76	0.396	*
Total	12.28	1.021	

* Unidentified compounds which are POM materials.

1. Sample Treatment

The total particulate matter collected in the trials at the copper reclaiming incinerator was collected and treated as follows:

a. The particulate matter from the probe and glass of the train was washed with pesticide quality toluene and combined with the particulate matter from filter.

b. This mixture was placed in a sonic bath for 1 hr to free the POM and PCB's.

c. The residue was removed via filtration and rinsed with 2 5-ml portions of toluene.

d. The filtrate, washings and the solutions from the impingers were evaporated to dryness.

e. The residue from this treatment was taken up in 0.2 ml of toluene.

f. Two microliters of extract were injected into a Perkin-Elmer Model 900 Gas Chromatograph under the conditions established in our laboratory for POM.

g. The compounds were identified via conventional gas chromatographic procedures.

h. The POM and PCB's were quantitated with know concentrations of standard materials.

2. Results

The results of our POM and PCB determinations on two consecutive runs were as follows:

Run # 1

POM = 5,145 $\mu g/m^3$
PCB = 1.13 $\mu g/m^3$

Run # 2

POM = 194.0 $\mu g/m^3$
PCB = 2.05 $\mu g/m^3$

The gas chromatographic data on POM and PCB's from these runs are summarized in Tables VI-IX.

3. Conclusions

Four runs in two separate field studies were conducted on this study. Two runs were made of Type II trash and copper wire insulation incinerated at high temperatures. These materials contained PCB's. The other 2 runs were conducted to determine PCB's and POM in burning rubber tires and PVC. In all runs, the collected particulate was analyzed for both POM and PCB's.

The following conclusions are presented:

a. Only 1 of the 5 POM's used in our laboratory studies was detected in the stack emissions from the burning of Type II trash. Nevertheless, the other compounds found in our analyses, closely resemble the other POM's. It is likely that these compounds are the oxygenated forms of the laboratory test compounds.

b. Coronene was identified in the stack emissions from the burning of copper wire insulation, rubber tires and PVC.

c. Even though specific PCB chromatographic peak ratios were not identical to conventional patterns, the electrophilic compounds producing these peaks possessed the proper retention times to indicate the presence of PCB's.

D. Field Study No. 5

A 2-week sampling program was conducted at the Kansas City, Missouri Municipal Incinerator. The emissions from the incinerator of sludge was monitored 16 separate times during the 2-week period from May 6 through May 20, 1974. No sampling problems were encountered; the runs were conducted as close to isokinetic conditions as possible in each experiment.

The analytical procedure followed after the stack gas samples were collected consisted of treating the particulate matter collected on the filter and the finer particulate and gases trapped in the probe and the bubblers of the POM train as separate samples. Each of these samples were individually extracted, analyzed by gas chromatography and evaluated for POM and PCB's. The results of these tests are summarized below from the data in Tables X and XI.

TABLE VI

SUMMARY OF GAS CHROMATOGRAPHIC DATA

Retention Times (min.)	POM & PCB Known Benzene Solution	Rubber	Oil	Grain	Polypropylene	Remarks
1.5	-	-	-	-	56.4	
1.8	-	-	-	-	-	Anthracene
2.0	-	-	-	-	60.6	
2.1	9.2	21.4	-	-	-	
2.8	-	-	-	-	58.2	
3.0	14.7	00.8	9.5	-	-	
3.6	-	12.4	-	2.9	-	
3.9	-	-	-	-	24.2	
4.1	*	*	*	*	*	Pyrene
4.5	-	-	-	-	26.6	
5.0	-	4.9	1.0	-	-	
5.8	7.4	39.6	1.0	2.2	38.8	
5.9	32.2	-	-	-	-	
6.7	-	-	-	-	38.8	
6.8	40.5	4.9	5.7	1.5	-	
8.0	81.1	42.9	58.9	52.4	60.6	BAA (7.4)
9.0	36.9	-	-	2.9	30.3	
9.1	-	6.6	-	-	-	
9.5	-	-	39.9	-	-	
10.2	73.7	19.8	39.9	16.4	24.2	
11.2	44.2	8.2	28.5	-	24.2	
12.2	-	-	-	-	12.1	BAP
12.4	44.2	-	-	-	-	
12.6	-	-	1.9	-	-	
12.8	-	-	-	10.9	-	
13.3	55.3	4.9	1.9	-	18.2	
14.5	77.4	6.6	1.9	-	10.9	
15.2	-	-	-	-	10.9	
15.4	29.5	-	-	-	-	
17.5	44.2	-	-	-	-	
18.5	-	-	-	-	4.8	
19.8	73.7	7.4	17.1	5.5	67.9	
21.8	18.4	-	-	-	7.3	
23.4	-	-	-	-	-	Coronene
24.0	-	-	-	-	3.6	
Total	683	180	207	95	579	

TABLE VII

SUMMARY OF AS CHROMATOGRAPHIC DATA
ON COPPER RECLAIMING INCINERATOR

Run # 1

	Retention Times (min)	POM (µg)	Retention Times (min)	PCB's (µg)
Anthracene →	3.1	1.9	1.0	0.79
	4.0	0.2	1.9	0.134
Pyrene →	5.3	2.4	2.2	0.06
	5.9	1.4	4.0	0.024
	7.0	3.4	5.2	0.206
Benz(α)Anthracene →	8.9	6,134	6.2	0.03
	11.6	2.2	7.8	0.009
	12.7	0.8	9.0	0.037
Benz(α)Pyrene →	13.8	5.2	10.0	0.037
	14.8	1.2	12.7	0.035
	15.8	4.2		
	16.9	4.0		
	17.7	5.7		
	19.0	4.5		
	19.9	5.7		
	22.0	13.6		
Coronene →				
TOTAL POM	6,190		TOTAL PCB	1.362

Run # 2

Anthracene →	1.9	0.8	1.0	0.388
	3.0	0.3	1.9	0.558
Pyrene →	4.0	0.2	2.2	0.012
	4.9	0.8	3.0	0.143
	6.0	0.4	3.4	0.298
	7.2	0.4	4.4	0.476
Benz(α)Anthracene →	8.2	0.6	5.0	0.018
	9.2	37	6.0	0.110
Benz(α)Pyrene →	13.7	204.9	7.0	0.229
	21.5	5.2	8.8	0.076
Coronene →			10.0	0.087
			11.0	0.023
			15.0	0.225
			23.0	0.019
TOTAL POM	250.6		TOTAL PCB	2.662

TABLE VIII

GAS CHROMATOGRAPHIC DETERMINATION OF POM'S
FROM (1) AND (2) BURNING TYPE II TRASH TO WHICH PCB'S WERE ADDED;
AND (3) AND (4) BURNING COPPER WIRE INSULATION, RUBBER TIRES AND PVC

Time Min.	Component	Amount (nanograms) No. 1	No. 2	No. 3	No. 4
1.4	Anthracene	-	-	-	-
3.2	Pyrene	-	-	-	-
4.1		1.53	-	-	-
4.8		30.23	3.07	8.20	6.15
5.8	Benz(α)Anthracene	-	-	-	-
5.9		437.46	53.68	130.36	80.51
6.8		-	1.73	11.50	9.59
7.2		34.51	18.40	16.10	7.67
8.0		5.18	6.63	-	6.63
8.2		-	-	-	6.63
8.6	Benz(α)Pyrene	-	-	-	-
8.7		4.15	4.98	12.43	3.32
9.2		-	2.49	27.36	4.98
9.7		-	-	9.95	3.32
10.2		-	2.49	32.33	-
10.7		-	-	7.46	-
11.2		-	-	25.23	-
11.6		-	-	5.41	-
12.4		-	-	6.76	4.51
13.2	Coronene	-	-	28.84	21.63
14.0		-	-	10.81	15.77
14.8		-	-	9.01	5.41
16.0		-	-	-	4.51
Totals		513.06	93.46	374.6	180.63

TABLE IX

GAS CHROMATOGRAPHIC DETERMINATION OF PCB'S
FROM (1) AND (2) BURNING TYPE II TRASH TO WHICH PCB'S WERE ADDED;
AND (3) AND (4) BURNING COPPER WIRE INSULATION, RUBBER TIRES AND PVC

Time	Amount (nanograms)			
Min.	No. 1	No. 2	No. 3	No. 4
1.0	-	19.7	-	-
1.2	12.7	6.6	13.2	82.2
1.5	-	-	-	9.9
1.7	12.7	3.3	13.2	6.6
2.2	-	-	-	29.6
2.9	-	58.6	9.9	82.7
3.2	7.0	4.0	-	-
3.5	-	4.8	9.6	-
3.7	1.6	17.4	-	27.2
4.4	12.4	-	-	63.9
4.7	-	27.9	21.6	-
4.9	67.0	-	-	4.0
5.5	12.0	75.4	-	19.2
6.1	87.8	21.5	20.4	121.0
6.8	-	-	-	252.9
7.2	-	55.7	14.5	369.6
8.2	8.6	-	-	-
9.1	-	82.0	200.9	225.0
10.0	10.7	-	-	21.4
10.6	-	54.6	-	-
11.7	39.1	-	13.0	3.9
12.1	-	-	-	59.2
13.0	253.4	83.3	16.3	-
14.0	-	-	-	3.9
14.6	-	134.8	-	-
15.0	-	-	-	5.9
15.2	-	-	-	3.9
15.8	15.6	-	78.1	-
16.6	-	-	-	78.1
18.2	-	-	-	2.0
19.0	78.1	-	-	-
20.0	-	32.6	-	1.3

TABLE IX (Continued)

Time Min.	Amount (nanograms) No. 1	No. 2	No. 3	No. 4
21.0	-	-	-	72.0
22.0	26.0	20.8	-	-
23.5	-	15.6	-	78.8
25.5	-	-	78.1	-
26.5	-	-	-	245.9
28.3	625.0	-	-	166.0
30.2	-	210.3	-	-
32.5	13.0	-	509.1	-
34.0	-	-	-	546.8
34.9	-	273.4	-	-
Totals	1,283.0	1,202.3	1,176.4	2,518.0

TABLE X

MICROGRAMS OF
POLYCYCLIC ORGANIC MATERIAL RESULTS
ON KANSAS CITY, MISSOURI SEWAGE TREATMENT PLANT

Relative Retention Time	Run 1 Filter	Run 2 Filter	Run 1 & 2 Bubbler	Run 3 Filter	Run 4 Filter	Run 3 & 4 Bubbler	Run 5 Filter	Run 6 Filter	Run 5 & 6 Bubbler
Anthracene			50.96			42.60			
10									
20			11.24						
30									
40									
50			11.24			9.47			9.48
60									
70									
80			57.08	4.39		15.40			5.14
90									
Pyrene			6.52			32.59			12.32
10						41.06			20.53
20							12.06		
30			6.52						
40						20.55			21.21
50				2.19					
60									7.95
70			11.01		3.56	35.57			17.78
80									
90						11.85			11.85

TABLE X (continued)

Relative Retention Times	Run 1 Filter	Run 2 Filter	Run 1 & 2 Bubbler	Run 3 Filter	Run 4 Filter	Run 3 & 4 Bubbler	Run 5 Filter	Run 6 Filter	Run 5 & 6 Bubbler
Benz(α)Anthracene			16.52	3.2	2.96			3.56	
10						17.78	46.42		
20			7.34	3.2					
30						5.93	57.63		
40			1.84	8.0		5.93			
50									
60									
70			8.78			11.86			
80				9.96					
90					2.82		149.37		
Benz(α)Pyrene				12.45					
							179.25		
10				4.98			169.29		
20				4.98			14.99		
30				4.98	2.82		14.99		
40							229.04		
50				14.94			248.95		
60									
70								12.17	
80									
90								12.17	
Coronene				20.90					
			4.80		12.17				
			2.56						
Total in micrograms			196.41	94.17	24.33	250.59	1,121.99	27.90	106.26

TABLE XI

MICROGRAMS OF
POLYCYCLIC ORGANIC MATERIAL RESULTS
ON KANSAS CITY, MISSOURI SEWAGE TREATMENT PLANT

Rel. Retention Times	Run 7		Run 8		Run 9	
	Filter	Bubbler	Filter	Bubbler	Filter	Bubbler
Anthracene		6.09		6.09		14.20
10						9.47
20						
30						
40						
50						
60						
70						
80						10.27
90	2.54	10.16		6.77		28.23
Pyrene		1.69		4.23		41.06
10	1.69					
20						20.53
30						
40						
50						
60						17.78
70			3.68	6.13		
80		6.13				
90						
Benz(α)Anthracene						23.71
10			2.45			
20	4.90		2.45			
30				2.45		11.86
40			2.45			
50						
60						
70						
80		2.58				
90						
Benz(α)Pyrene	5.15					
10		5.15		5.16		
20						
30			6.44			
40						
50				6.45		
60						
70						
80						
90						
Total in Microgram:	14.28	31.80	17.47	37.28	0	177.11

TABLE XI (continued)

Rel. Retention Times	Run 10		Run 11		Run 12		Total Wash
	Filter	Bubbler	Filter	Bubbler	Filter	Bubbler	
Anthracene				20.53		10.27	
10							
20	1.70			9.47			
30							
40						4.74	
50							
60							
70							
80		5.13		10.27		15.41	10.28
90							
Pyrene		20.53		20.53		20.53	30.8
10		20.53		30.80		38.50	43.63
20		5.13					
30	2.19						
40				15.40		15.41	31.82
50							
60		29.64					23.71
70				23.71		23.71	17.70
80	3.20						
90		11.86				8.89	11.85
Benz(α)Anthracene		11.86					
10				17.78			65.18
20							
30				11.86		23.72	
40		17.78		5.93		8.90	
50							
60							
70						17.79	
80							
90					4.98		23.72
Benz(α)Pyrene	4.98						
10	9.96						
20	34.85						
30	29.87						
40							
50							121.67
60							30.42
70							30.42
80							
90							
Total in Micrograms	86.75	122.46	0	166.28	4.98	187.87	441.2

1. Summary of Test Results

Run No.	Concentration of POM in Particulate (%)	Conc. of POM in Gas ($\mu g/m^3$)	Concentration of PCB in Particulate (%)	Conc. of PCB in Gas ($\mu g/m^3$)
1 & 2	0.283	74.91	0.0058	1.54
3 & 4	0.864	140.64	0.021	3.42
5 & 6	0.980	487.63	0.0033	1.66
7	0.141	34.98	0.0090	2.24
8	0.198	41.70	0.0035	0.75
9	0.542	137.46	0.0143	3.64
10	0.421	156.54	0.0174	6.47
11	1.08	126.86	0.0293	3.71
12	1.24	147.00	0.0435	5.16

2. Conclusions

a. Satisfactory analytical data was obtained during these inventories because the operating conditions of the plant and the composition of the sludge varied minimally.

b. More POM was found on the filter paper, especially the higher molecular weight materials between benz(α)pyrene and coronene than that identified in the bubblers.

c. The amount of total particulate matter was relatively small yet the POM content in this collected particulate was extremely high.

d. The PCB's identified possessed a very high molecular weight (greater than pyranol).

e. The POM's which were selected for this program were present in the samples collected.

f. Even though identification of POM's and PCB's was not confirmed with other analytical methods, past experiences and a thorough evaluation of the gas chromatographic data indicate that the POM and PCB materials of the gas-particulate system are present.

E. Field Study No. 6

The last field experiment, a 2-week sampling program, was conducted at a prominent charcoal burning restaurant in the Kansas City SMSA.

This operation was monitored over the 2-week period from June 9 through June 23, 1974 with 13 runs. Even though erratic and turbulent flow occurred in the stacks, the probe gases were continually adjusted to adher to near isokinetic conditions.

The analytical procedure followed after the stack gas samples were collected consisted of treating the particulate matter collected on the filter and the finer particulate and gases trapped in the bubblers of the POM trains as separate samples. Each of the samples was individually extracted, analyzed by gas chromatography and evaluated for POM and PCB's. The results of these tests are summarized in Tables XII and XIII.

The conclusions obtained from these results are as follows:

a. The analytical data on this inventory varied daily because the operating conditions of the stack and the operations of the restaurant varied considerably.

b. An extremely large amount of POM was found on the filter paper.

c. The relative level of total particulate matter to materials in other parts of the train was found to be much higher than found at other stationary sources, the POM content in the collected particulate was extremely high.

d. The PCB's identified in these stack gases were similar to Arochlor 1242, rather than the higher molecular weight Arochlor 1254 or higher.

e. The POM's which were selected for this program were identified to be present in the samples collected.

f. As in other field inventories, the identification of POM's and PCB's was not confirmed with other analytical techniques. However, based on past experience and a thorough evaluation of the gas chromatographic data, the POM and PCB of the gas-particulate system on this study is present.

TABLE XII

SUMMARY OF RESULTS OF 13 RUNS FOR POM
IN THE STACK GASES OF A CHARCOAL BURNING RESTAURANT

G.C. Retention Time (min.)	Average Amount of POM's in Nanograms Collected			
	Minimum Volume Collected (1)	Maximum Volume Collected (2)	Average Collected in Particulate Fraction	Average Collected in Bubblers
1.0	50.9	-	-	-
1.8	144	-	-	-
1.9 - Anthracene	-	-	-	-
2.2	153	17.0	21.2	-
3.0	204	4.2	7.1	-
3.9	171	-	-	4.8
4.2	400	-	130.9	4.8
4.4	457	-	-	-
4.5 - Pyrene	-	-	-	-
5.0	-	100	71.4	-
5.2	-	78.5	59.5	-
5.5	114	-	23.8	-
5.9	-	-	23.8	4.8
6.4	165	30	-	-
6.8	-	-	150	-
7.2	60	143	12.5	5.0
8.0 - BAA	-	45	68.8	-
8.8	-	15	18.8	-
9.0	-	22.5	-	15.0
10.0	60	-	-	5.0
11.0	63	8	13.1	2.6
11.9 - BAP	-	-	19.7	2.6
12.3	16	-	13.1	-
12.5	-	-	19.7	2.6
13.1	204	16	-	2.6
14.2	189	-	-	-
14.7	-	-	26.2	-
15.0	16	-	-	-
15.8	236	63	-	-
18.0	-	-	26.2	-
18.2 - Coronene	23	-	-	-
19.2	35	-	-	-
Total	2,761	542	705.8	49.8

TABLE XIII

SUMMARY OF RESULTS OF 13 RUNS FOR PCB'S
IN THE STACK GASES OF A CHARCOAL BURNING RESTAURANT

G.C. Retention Time (min.)	Average Amount of PCB's in Nanograms Collected			
	Minimum Volume Collected (1)	Maximum Volume Collected (2)	Average Collected in Particulate Fraction	Average Collected in Bubblers
2.75	68.5	11,424	465	29.4
3.5	-	1,044	-	-
3.9	80	1,828	245	36.7
4.5	22.8	1,632	33	67.3
4.95	-	-	-	14.7
5.2	430	5,222	2,074	422
5.8	-	-	102	-
6.3	358	3,584	230	-
7.2	108	-	307	34.6
8.4	-	1,434	-	-
9.2	376	614	-	-
10.8	288	-	69	10.3
11.2	-	219	-	-
14.0	80	206	123	14.4
15.4	50	-	113	-
16.2	-	61.8	-	-
17.5	-	34.2	-	-
18.9	-	274	-	-
21.0	-	891	-	-
Total	1,861	28,468	3,761	629.4

81.57 ft^3 sampled = 2.32 m^3
wt. collected on filter paper Run # 1 = 0.0561 g

105.51 ft^3 sampled = 3.00 m^3
wt. collected on filter paper Run # 2 = 0.4140 g

VIII. FUTURE STUDIES

During the program, we have recognized several areas which should be investigated further by the Environmental Protection Agency. These areas are summarized below:

1. Conduct an Industrial Study: The objectives of this survey would be to more clearly define the extent of the problem, establish a list of critical industries which could possibly be POM and PCB polluters, and obtain more statistical data on practical applications of the sampling techniques obtained from this program.

2. Investigation of Other Sources: The objective of this study would be to conduct a parallel study on PCB and POM as contaminants in water, waste water, solid waste and commercial products and materials.

3. Investigation of Abatement Practices: The objective of this investigation would be to challenge various treatment and abatement systems to resolve any problems where they may exist.

4. Further Analytical Studies: The objective of these studies would be to identify and evaluate an acceptable standard analytical procedures for determining residual PCB and POM. In this program GC and LLC (with different detectors), TLC, column cleanup, gel permeation (molecular weight), extraction preparation and mass spectroscopy should be evaluated.

We feel that possibly a combination of some of the critical aspects of these ideas could be pursued in an effort to organize what might be a future routine procedure employed by federal, state, municipal, industrial, and independent field teams. This work would involve a systematic effort to first more clearly define what of the many POM and PCB's of carcinogenic nature are predominant as an industrial pollutant. We would then define the minimum detectable limit of the best sampling and analytical procedure available. The laboratory analytical procedure would be more critically evaluated and finally an organized and concise publication would be made for an official EPA approach to the sampling. Analytical requirements would be included in this paper to describe the specific POM and PCB content in gas flows as well as water.

BIBLIOGRAPHY

1. E. Sawicki, Arch. Environ. Health, 14, 46 (1967)

2. R. P. Hangebrauck, D. J. von Lehmden, and J. E. Mecker, "Sources of Polynuclear Hydrocarbons in the Atmosphere," U. S. Public Health Service Publ. No. 999-AP-33, Cincinnati, Ohio (1967).

3. D. Hoffmann and E. L. Wynder in "Air Pollution," Vol. II, 2nd Edition, Chapter 20, A. C. Stern, Editor, Academic Press, New York (1960).

4. G. M. Badger, Nat'l. Cancer Inst. Monograph, 9, 1 (1962).

5. G. M. Badger, J. K. Donnelly, and T. M. Spotswood, Australian J. Chem., 19, 1023 (1965).

6. I. E. Burrows and A. J. Lindsay, Chem. and Industry (London), 1395 (1961).

7. J. R. Newsome and C. H. Keith, Tobacco Sci., 9, 65 (1965).

8. R. Long, et al., "Formation of Polycyclic Aromatic Hydrocarbons During Incomplete Combustion," APTIC Document No. 5325, March 1967.

9. P. Kotin and H. L. Falk, Adv. in Cancer Res., 7, 475 (1963).

10. D. F. Bender, E. Sawicki and R. M. Wilson, Anal. Chem., 36, 1011 (1964).

11. L. Dautrebande, H. Beckman and W. Walkenhorst, A.M.A. Arch. Ind. Hyg., 16, 179-187 (1957).

12. B. L. VanDuuren, L. Orris and N. Nelson, J. Nat'l. Cancer Inst., 35, 707 (1965).

13. R. J. Cvetanovic, Can. J. Chem., 37, 953 (1959).

14. E. Sawicki, J. E. Mecker and M. J. Morgan, Air Water Pollution, 9, 291 (1965).

15. E. Sawicki, J. E. Mecker and M. J. Morgan, Arch. Environ. Health, 11, 773 (1965).

16. E. Sawicki, S. P. McPherson, T. W. Stanley, J. Mecker and W. C. Elbert, Int. J. Air Water Pollution, 9, 515 (1965).

17. D. F. Bender, E. Sawicki, and R. M. Wilson, Int. J. Air Water Pollution, 8, 633 (1964).

18. E. L. Wynder and D. Hoffman, "Tobacco and Tobacco Smoke," Academic Press, New York (1967).

19. D. J. Hansen, et al., Bull. Environ. Contamin. & Tox., 6 (2), 113 (1971).

20. V. Goppers and H. J. Paulus, Amer. Ind. Hyg. Assoc. J., 23, 181 (1962).

21. R. S. Tipson, A. Cohen, and A. J. Fatiadi, NBS Technical Note 427, 11, October 1967.

22. E. Sawicki, T. W. Stanley, T. R. Hauser, H. Johnson and W. Elbert, Int. J. Air Water Pollution, 7, 57 (1963).

23. W. Troll, Analytical Chem., 41, 22A (1969).

24. E. Sawicki, Chemist-Analyst, 53, 24, 28, 56, 88 (1964).

25. E. Sawicki, T. W. Stanley, W. C. Elbert, J. Mecker and S. McPherson, Atmos. Environ., 1, 131 (1967).

26. E. Sawicki, J. L. Noe and F. T. Fox, Talanta, 8, 257 (1961).

27. K. Wettig, Neoplasma, 14, 181 (1967).

28. R. L. Stenburg, D. J. von Lehmden, and R. P. Hangebrauck, Amer. Ind. Hyg. Assoc. J., 22, 271 (1961).

29. T. W. Stanley, J. E. Mecker, and M. J. Morgan, Environ. Sci. Tech., 1, 927 (1967).

30. L. Dubois, A. Zdrojewski, and J. L. Monkman, Mikrochim Acta, 5, 903 (1967).

31. E. P. Aizina and I. M. Mints, Hygiene and Sanitation, 31, 264 (1966).

32. G. E. Moore, R. S. Thomas, and J. L. Minkman, J. Chromatography, 26, 456 (1967).

33. L. Dubois, A. Zdrojewski, C. Baker and J. L. Monkman, J. Air Pollution Control Assoc., 17, 818 (1967).

34. E. Sawicki, H. Johnson and K. Kosinski, Microchemical J., 10, 72 (1966).

35. E. Sawicki, T. W. Stanley, and W. C. Elbert, J. Chromatography, 18, 512 (1965).

36. E. Sawicki, W. Elbert, T. S. Stanley, T. R. Hauser and F. T. Fox, Int. J. Air Pollution, 2, 273 (1960).

37. E. Sawicki, W. Elbert, T. W. Stanley, T. R. Hauser, and F. T. Fox, Anal. Chem., 32, 810 (1960).

38. R. H. White and J. W. Howard, J. Chromatography, 29, 108 (1967).

39. G. Lindstedt, Atmos. Environ., 2, 1 (1968).

40. E. Sawicki, C. R. Engel, and W. C. Elbert. Talanta, 14, 1169 (1967).

41. E. Sawicki, T. W. Stanley, and W. C. Elbert, Talanta, 14, 431 (1967).

42. B. B. Chakraborty and R. Long, Environ. Sci. and Tech., 1, 828 (1967).

43. V. Cantuti, G. P. Cartoni, A. Liberti, and A. G. Torri, J. Chromatography, 17, 60 (1965).

44. N. Carugno and S. Rossi, J. Gas Chromatography, 5, 103 (1967).

45. L. DeMaio and M. Corn, Anal. Chem., 38, 131 (1966).

46. J. R. Wilmhurst, J. Chromatography, 17, 50 (1965).

47. L. S. Ettre, R. D. Condon, F. J. Kabot, and E. W. Cieplinski, J. Chromatography, 13, 505 (1964).

48. E. Sawicki, M. Guyer, R. Schumacher, W. C. Elbert, and C. R. Engel, Mikrochim. Acta, 5, 1025 (1968).

49. J. Finklea, et al., AJPH, 62 (5) 645 (1972).

APPENDIX

PROCEDURE FOR THE DETERMINATION OF POM AND PCB'S

1. Principle

1.1 Principle. Polynuclear organic matter (POM) and polychlorinated biphenyls (PCB) are withdrawn isokinetically from the source and determined gas chromatographically.

2. Apparatus

2.1 Sampling Train. The design specifications of the POM train (Figure 1) are described in the main body of the report. Slight modifications of the EPA Method 5 train will produce the required assembly.

2.1.1 Nozzle - Stainless steel (316) with sharp, tapered leading edge.

2.1.2 Probe - Pyrex[1] glass with a heating system capable of maintaining a minimum gas temperature of 250°F at the exit and during sampling to prevent condensation of water from occurring. When length limitations (greater than about 8 ft) are encountered at temperatures less than 600°F, Incoloy 825[1] or equivalent, may be used. Probes for sampling gas stream at temperatures in excess of 600°F must have been approved by the Administrator.

2.1.3 Pitot Tube - Type S, or equivalent, attached to probe to monitor stack gas velocity.

2.1.4 Filter Holder - Pyrex[1] glass with heating system capable of maintaining minimum temperature of 225°F.

2.1.5 Impingers/Condensor - Five impingers (modified Greenburg-Smith design) are connected with glass ball joint fittings. Impingers # 1 and # 2 are connected to the filter holder with a T connector. Impingers # 3 and # 4 are connected to Impingers # 1 and # 2 with U connectors and to Impinger # 5 with a T connector. (See Figure 1)

2.1.6 Metering System - Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5°F, dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer - To measure atmospheric pressure to $\pm$ 0.1 inches Hg.

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[1] Trade Name

2.2 Sample Recovery

2.2.1 Probe Brush - At least as long as probe.

2.2.2 Glass Wash Bottles - Two.

2.2.3 Amber glass storage bottles.

2.2.4 Graduated Cylinder - 100 ml.

2.3 Analysis

2.3.1 Gas Chromatograph - Flame Ionization Detector

Column - 6 ft x 1/8 in., 6% Dexsil 300 GC on 80/100 Chromosorb "W" H/P*

Carrier - N_2 - 80 psig, flowmeter at 2.0 mg/min

Air - 39 psi H_2 - 35 psi

Program - 1. Start at 170°C hold 8 min.
2. 12°C/min at 320°C.
3. Hold

Peak Identification -	6 min	223.2×10^{-6} g	Anthracene
	12.4 min	192.3×10^{-6} g	Pyrene
	15.6 min	188.0×10^{-6} g	Benz(α)Anthracene
	18.5 min	406.6×10^{-6} g	Benz(α)Pyrene
	24.1 min	362.4×10^{-6} g	Coronene
	3.1 min	$1,633 \times 10^{-6}$ g	Arochlor 1242

* Mention of trade name or commercial products does not constitute endorsement or recommendation by EPA.

2.3.2 Kuderna-Danish concentrator

2.3.3 Steam bath

3. Reagents

3.1 Sampling

3.1.1 Filters - Glass fiber MSA 1106 BH,[1] or equivalent, numbered for identification and preweighed.

3.1.2 Silica Gel - indicating type, 6-16 mesh, dried at 175°C (350°F) for 2 hours.

3.1.3 Xylene - analytical reagent grade

3.1.4 Crushed ice

3.2 Sample Recovery

3.2.1 Xylene - reagent grade

3.3 Analysis

3.3.1 Xylene - reagent grade

3.3.2 Silica gel as in 3.1.2

4. Procedure

4.1 Sampling

4.1.1 Select the sampling site and the minimum number of sampling points according to Method 1 and determine the stack pressure, temperature, moisture and range of velocity head according to Methods 2 and 5.

4.1.2 Preparation of Collection Train. Place 100 ml of xylene into the first four impingers and place ~ 200 g of silica gel covered with glass wool in the fifth impinger. Set up the train as in Figure 1 without the probe. Leak check the sampling train at the sampling site by plugging up the inlet to the filter holder and pulling a 15 inch Hg vacuum. A leakage not in excess of 0.02 cfm at a vacuum of 15 inch Hg is acceptable. Attach the probe and adjust the heater to provide a gas temperature of ~ 250°F at the probe outlet. Turn on the filter heating system. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger as low as possible and preferably at 70°F.

4.1.3 POM Train Operation. Take readings at each sampling point, at least every 5 min. and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 min. at each traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD-0576 details the procedure for using these nomographs. Turn off the pump at the conclusion of each run and record the final readings. Remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in Section 4.2.

4.2 Sample Recovery. Exercise care in moving the collection train from the test site to the sample recovery area to minimize the loss of collected sample or the gain of extraneous particulate matter. Set aside a portion of the xylene used in the sample recovery as a blank for analysis. Combine the contents of the first four impingers with the filter and rinsings of the probe, cyclone, and connectors in a glass bottle and place bottle in a sonic bath for ~ 1 hr, filter the contents of the bottle into a Kuderna-Danish concentrator, rinsing the filter with 3 successive 25 ml portions of xylene. Evaporate the contents to dryness. Take the residue up to 0.2 ml xylene.

5. Calibration

Use method and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater. Recalibrate after each test series.

6. Calculations

6.1 Average dry gas meter temperature and average orifice pressure drop.

6.2 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (70°F, 29.92 inches Hg) by using Equation 1.

$$V_{m_{std}} = V_m \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}\right) = \left(17.71 \frac{^\circ R}{\text{in. Hg}}\right) V_m \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m}\right)$$

Equation 1

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu ft

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu ft

T_{std} = Absolute temperature at standard conditions, 530°R.

T_m = Average dry gas meter temperature °R

P_{bar} = Barometric pressure drop at the orifice meter, inches Hg

ΔH = Average pressure drop across the orifice meter, inches H_2O

13.6 = Specific gravity of mercury

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg

6.3 Total POM's and PCB's. Determine the POM and PCB content by injecting 2 µl of the extract into a gas chromatograph at the conditions described in 2.3.1

6.4 Concentration

6.4.1 Concentration in µg/scf

$$C_s' = \frac{M_n}{V_{m_{std}}}$$

where:

C_s' = Concentration of specific POM or PCB or total in stack gas, µg/scf, dry basis

M_n = Specific POM or PCB or total found in µg

$V_{m_{std}}$ = Volume of gas sampled through dry gas meter (standard conditions), cu ft

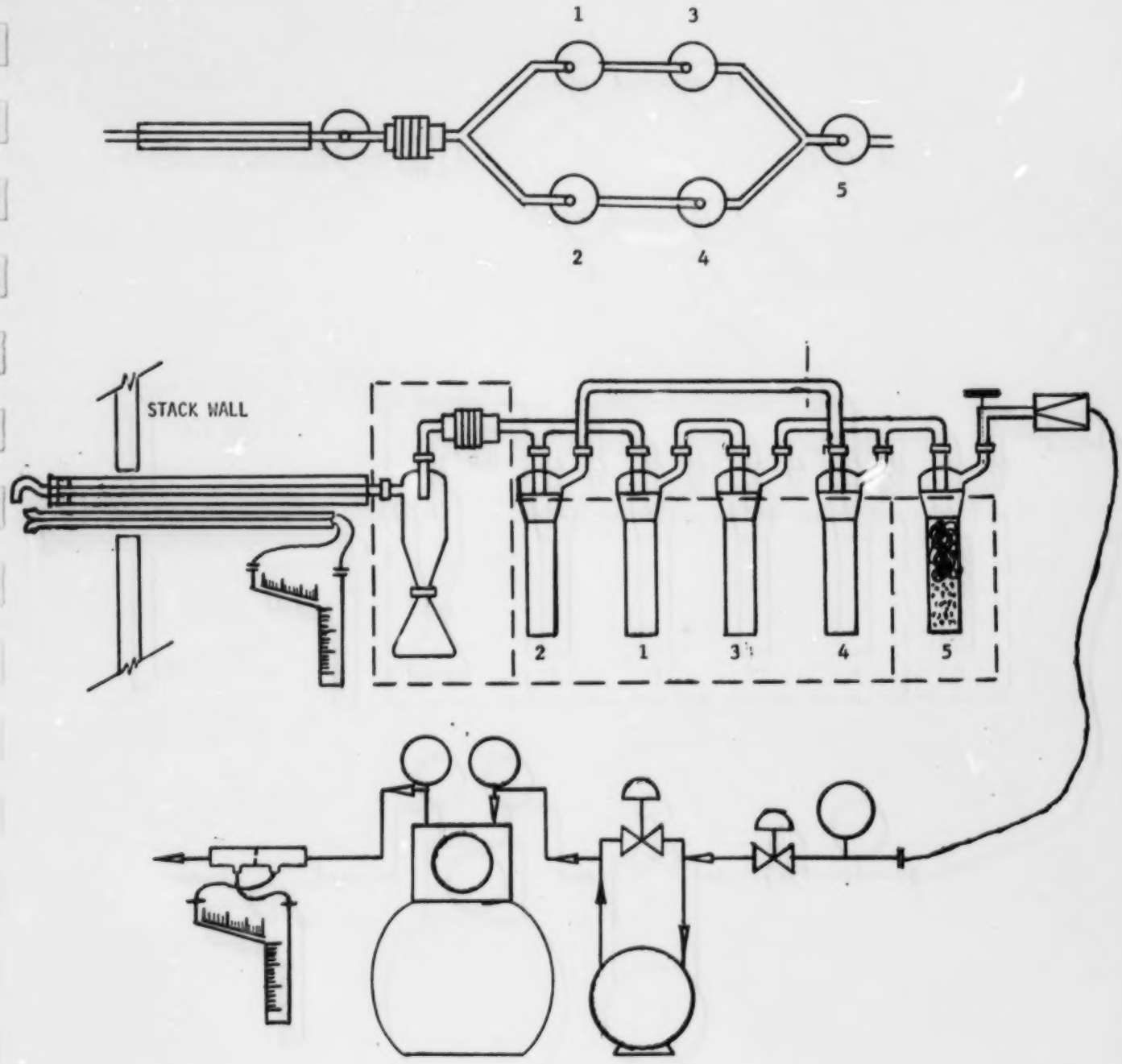

Figure 1 - POM Train